PHOTOLYSIS OF COPOLYMERS IN SOLUTION

A thesis submitted to the University of Glasgow for the degree of Doctor of Philosophy in the Faculty of Science

by

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The work described in this thesis was carried out in the period October 1969 to August 1972 at the University of Glasgow, in the Department of Physical Chemistry which was formerly under the direction of Professor J.M. Robertson, C.B.E., F.R.S., and latterly under the direction of Professor G.A. Sim, B.Sc., Ph.D.

Part of the work has been published in Chemické Zvesti 26, 200 (1972) and a reprint of this paper has been included at the end of the thesis.

I wish to express my gratitude to Professor N. Grassie for suggesting the problem and for his guidance and encouragement throughout the course of this work.

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CONTENTS

Summary of Ph.D. thesis,

Photolysis of Copolymers in Solution. T. Irwin Davis.

Preliminary investigations of the photolysis of poly-(methyl acrylate) homopolymer in solutions of methyl acetate, chloroform, methylene chloride and benzene were carried out. The light source employed was a Hanovia Chromatolite Lamp which produces, primarily, radiation of wavelength 2537Å. The resulting chain scission reaction of the polymer was followed by monitoring the change in molecular weight of the polymer samples after varying periods of irradiation. Molecular weight analyses were determined using a Mechrolab High Speed Membrane Osmometer.

The rate of chain scission of poly-(methyl acrylate) in solution was found to be independent of polymer concentration over the range 1 - 10% W/V, and to be little affected by the solvent used, other than that expected from optical filtering considerations.

The two homopolymers of methyl methacrylate and methyl acrylate and a series of copolymers covering the entire composition range were prepared and the photodegradation of solutions of these samples was carried out. The characteristics of the photo-induced chain scission reaction across the composition range were studied and compared with those observed in the photolysis of thin films of the same polymer system. Differences observed, in particular an enhanced rate of chain scission of poly-(methyl methacrylate) in solution compared with that found in film photolysis, have been explained in terms of Glass Trans-

ition Temperatures.

Photo-oxidation has also been carried out with both thin films and solutions of these polymer samples and the relative degradation characteristics have been compared. Differences observed have been rationalised in terms of the subsequent reactions available to the polymer radicals obtained after the initial photo-induced cleavage of the ester side groups.

Copolymers of methyl methacrylate with methacrylonitrile and styrene, covering the entire composition ranges, were prepared and irradiated in solution with methylene chloride. Methacrylonitrile, being structurally very similar to methyl methacrylate did not appear to have a significant effect upon the rate of chain scission of methacrylate-rich copolymers but it has been shown that the strong radiation-absorbing benzenoid nucleus of the styrene comonomer has a protective effect upon methacrylate-rich copolymers due to preferential absorption of the degradative radiation at stable aromatic sites.

Some copolymers of methyl methacrylate and maleic anhydride were prepared and it has been shown that incorporation of even a very small quantity of maleic anhydride as comonomer greatly enhances the rate of the photo-induced chain scission reaction of methacrylate-rich copolymers.

CHAPTER 1.

INTRODUCTION.

It has long been recognised, almost since polymers first became commercially significant, that their resistance to ultra-violet radiation is an extremely important factor in determining their useful life. The commercial importance of the degradative effects of radiation and the comparitively more recent interest in the more fundamental interaction of radiation with matter have together stimulated interest in the photodegradation of polymers in the past decade.

In most work, mercury vapour lamps have been used as the source of ultra-violet radiation. Low pressure "germicidal" lamps are a convenient, relatively monochromatic low intensity source of 2537Å radiation. Medium pressure lamps provide radiation at a number of wavelengths in the 2200-4000Å region, any particular wavelength being readily isolated by the use of filters. High pressure lamps give high intensity radiation over a continuum of wavelengths in the same region. These and other ultra-violet radiation sources have been

described in detail.[1,2] Determination of the intensity of the incident radiation from these sources can be effected by conventional uranyl oxalate actinometry[1,3,4] or by the more rapid ferrioxalate method.[2,5,6]

Photodegradation reactions can be studied in solution or with bulk polymers in thin film or powder form, quartz photolysis cells usually being used as reaction vessels. Polymer purity is always a problem. Jellinek and Bastien[7] noted that sample history had a marked influence on the course of the photolysis reaction of polyacrylonitrile in solution. Isaacs[8] observed large variations in quantum yield for hydrogen formation from polystyrene films cast from different chlorinated solvents.

Determination of molecular weight changes in the polymer sample is the usual method of following the course of photodegradation reactions. Viscometry is the most widely used technique, although light scattering and osmometry are commonly applied to the study of copolymer degradation due to the lack of available viscometry parameters for copolymer systems. Where the polymer undergoes crosslinking, gel fraction studies are often used. Volatile products from the photolysis of solid polymers are usually analysed by spectroscopic techniques,

mass spectrometry and gas chromatography. Evolution of volatiles during degradation may be followed with a pressure measuring device such as a Pirani gauge or by manomeric techniques. This thesis is concerned with the effect of ultra-violet radiation from a low pressure mercury vapour lamp on solutions of copolymers, containing methyl methacrylate as one of the comonomers. The progress of the reactions was monitored by determining molecular weight changes using the technique of osmometry.

Theoretical Considerations.

Photolytic degradation is brought about by the absorption of energy in the form of photons. This causes the formation of free radicals which ultimately lead to changes such as main chain scission, crosslinking, unsaturation and the formation of small molecules.

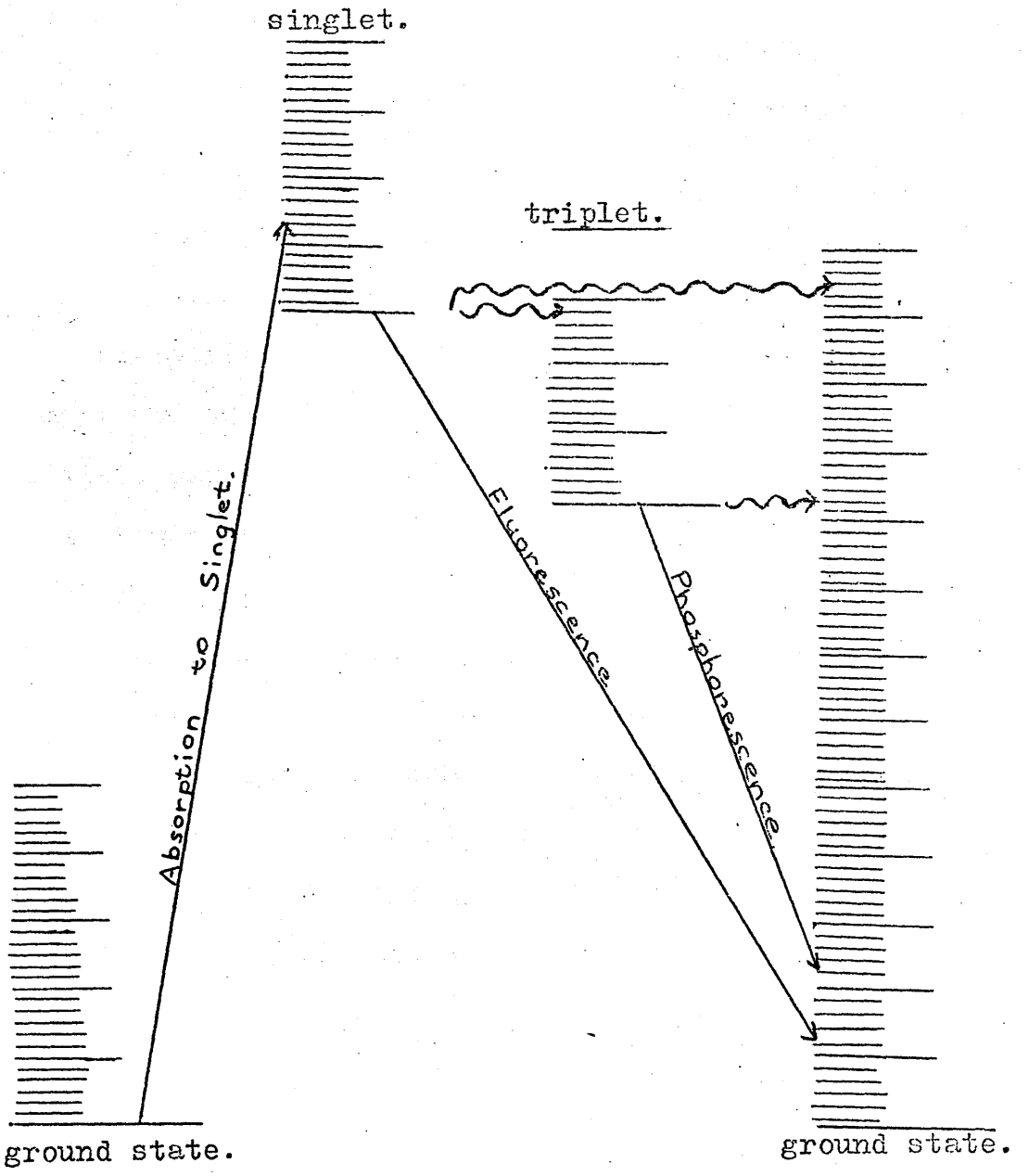
Most organic molecules lie in a singlet ground state. After absorption of a photon to give an excited singlet state, the molecule may revert to the ground state by emission of a photon(fluorescence) or by radiationless transitions and the generation of heat. In some instances, intersystem crossing can take place, and the molecule will shift to an excited triplet level of lower energy.

Again the reversion to the ground state may be accompanied by photon emission(phosphorescence) or heat. If the molecule has sufficient energy in the excited state, either the singlet or the triplet, dissociation or rearrangement may take place. Reversion to the ground state may also be accomplished by transfer of energy between the excited molecule and a second molecule. These processes are illustrated in fig.1.1. Radiationless transitions are favoured in complex molecules[9] and processes involving such intramolecular energy transfer are the most likely route to photodissociation.

Photochemical data are probably more extensive for compounds containing a carbonyl group than for any other class of organic compounds. Most work has been carried out on aldehydes and ketones but, broadly speaking, acids, acid anhydrides, esters and even amides undergo analogous photodissociative reactions. R.G.W. Norrish[10] and his co-workers were the first to make a systematic study of the photochemistry of molecules containing the aldehyde and ketone functional groups. Among polymeric ketone derivatives, polymethylvinylketone has been shown[11] to undergo simultaneously, Norrish I and II processes in

Fig.1.1. JABLONSKI DIAGRAM.

Photophysical Transitions.



Solid lines = radiative transitions.

Wavy lines = radiationless processes.

solution[12] and the solid state. The photolysis of polymethylisopropenylketone leads to main chain cleavage[14] followed by depolymerisation between 130°C and 180°C[13]. However, the model compound for polyphenylvinylketone, butyrophenone, has been found to undergo mainly Norrish Type 1 cleavage. In benzene solution, however the polymer was found to undergo mainly Norrish Type 11 cleavage leading to chain scission.

Photolytic processes can be separated into 2 groups- primary and secondary. Primary processes involve the immediate excitation effect of the light on the absorbing molecule, deactivation through fluorescence, heat emission, energy transfer etc., or destruction by transformation of the starting material into new compounds, whereas secondary processes are the reactions of the molecules, atoms or radicals produced as a result of the primary process. It is important to remember that, because the absorbed energy may be transferred intramolecularly, the site at which the ultra-violet light is absorbed may not necessarily be the site at which bond rupture takes place. If the energy of excitation is greater than, or equal to, the bond dissociation energy

of the weakest link in a molecule then cleavage may occur. Bond dissociation in polymers may lead to a chain scission, this being one of the two principal reactions involving the polymer backbone, the other being crosslinking.

The reactions occurring in a polymer undergoing photolysis may be classified as direct or indirect. Direct reactions come about from the absorption of a photon by the polymer, followed by bond homolysis and the formation of degradation products. When substances other than the polymer undergoing photolysis are present, indirect reactions can occur. These "foreign" molecules, whether they are solvent molecules, small molecular impurities, added sensitisers or inhibitors can similarly be excited and undergo reactions to form free radicals. These excited molecules or fragments may eventually interact with the polymer to give products similar to those arising from the direct processes. The reverse reactions may also occur; excited polymer molecules or polymer radicals may interact with the "foreign" molecules.

$$P_{n+m} + S^{*} \rightleftharpoons S + P^{*}_{n+m}$$

$$P_{n+m} + S^{\bullet} \rightleftharpoons S + P^{\bullet}_{n+m}$$

An obvious example of an indirect reaction is the effect of atmospheric oxygen on polymer photodegradation. with regard to chain scission oxygen can play the role of apparent inhibitor, as in polystyrene or seemingly be without influence as in poly-(α-methyl styrene).[15] Other examples are the influence of sensitisers on the cross-linking of polyolefins[16] and the effect of residual solvents in polymer films.[8] The existence of an indirect effect is readily seen in the photodegradation of polymers in solution. Apparent quantum yields for the random scission of poly-(α-methyl styrene)[17] and poly(methyl methacrylate) are markedly dependent on the solvent[18].

Reactions of the Polymer Chain.

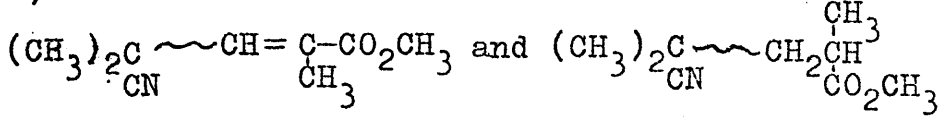
1. Chain Scission.

a. Initiation.

In general, initiation occurs either at random or at specific chain terminal structures. In random initiation, chain scission occurs at random points along the chain, giving radicals which tend to be large compared to a monomer unit. Samples of reactions in which random initiation is thought to occur are the room temperature photolytic degradation of poly-(methyl methacrylate)[19],

the photodegradation of poly-(α-methyl styrene)[20] and the thermal degradation of polybutadiene.[21] Weak links (bonds in the polymer chain which are more susceptible to chain scission than normal) have often been postulated[22] but the existance of these weak links has usually been questioned.[23]

In the second initiation mechanism, end initiation, the bonds occurring at the ends of the chain are particularly vulnerable and are thus exclusively broken. The result is the formation of a long chain polymer radical along with an end group radical. The end group in polymers can vary considerably depending on the initiator used in the polymerisation and the type of termination which occurs. For example, azo-bis-isobutyronitrile catalysed polymerisations of methyl methacrylate, in absence of transfer and assuming termination by disproportionation, will give molecules having at one end a catalyst fragment and at the other , either a saturated or an unsaturated structure formed in the disproportionation,



Half the polymer molecules will be of one form, half of the other. Any end initiation should take place at the unsaturated end as the C—C bond adjacent to the C=C bond is more vulnerable than the others. Reactions in which end initiation is thought to take place include the high temperature photodegradation of poly-(methyl methacrylate)[24] and the thermal degradation of the same polymer[25].

b. Subsequent Reactions.

The radicals formed by chain scission may "peel off" monomer molecules or depropagate. Whether the decomposition of a particular material will result in a high monomer yield depends in the first place on the production of the necessary radicals in the initiation process. Following the initiation, one of several things may happen. One possibility is a rapid decrease in molecular weight without any monomer being given off. There is no unzipping (depropagation) as other reactions are predominating. Volatiles other than monomer may be evolved however. Most room temperature photolytic degradations are of this type. A second possibility is partial unzipping in which small amounts of monomer are formed.

In such a case, either a fraction of the chains depropagate as in the thermal degradation of poly-(methyl methacrylate) below 220°C [22], or termination has prevented the reaction going to completion as in the photolytic degradation of poly-(α-methyl styrene) [20] at 115°C. The final possibility is complete unzipping in which large amounts of monomer are evolved as the chains completely depropagate. There is no termination. For end initiation the molecular weight of the residue will remain nearly constant, or may even rise slightly [22] if more rapid degradation of low molecular weight material occurs. Random initiation will give a different result. The molecular weight will decrease rapidly before any significant conversion to monomer occurs. The extent and rate of decrease will depend a great deal on the distribution of molecular weights within the sample [26]. Examples of complete unzipping include the thermal degradation of poly-(methyl methacrylate), especially low molecular weight samples, at temperatures well above 220°C, and the photolytic degradation of poly-(methyl isopropenyl ketone) at 150°C [27].

The extent of unzipping depends on the polymer

involved and the conditions of the degradation reaction. In many degradation reactions there is a temperature below which no depropagation will occur. Above this temperature there is unzipping which may increase as the temperature increases. This floor temperature for depropagation is related to the ceiling temperature for polymerisation - the temperature above which the corresponding polymerisation does not occur[22]. The existence of these temperatures is due to the reversibility of the propagation and depropagation reactions;

$$P_n + M \underset{\text{depropagation}}{\overset{\text{propagation}}{\rightleftharpoons}} P_{n+1}$$

Below the floor temperature, the propagation reaction will be favoured. Between the floor and ceiling temperatures, monomer and polymer exist in equilibrium and above the ceiling temperature the depropagation reaction will be favoured. Ceiling temperatures for thermal (propagation - depropagation) reactions are quite high (~300°C for styrene)[22] but those for photo-induced (propagation-depropagation) reactions tend to be much lower. A great deal of the work on monomer-polymer equilibria was carried out by Dainton and Ivin[28-31] who were the first to explain ceiling temperatures in terms of propagation-

depropagation reactions.

2. Crosslinking.

Under some circumstances, ultra-violet radiation can cause crosslinking which leads to a three dimensional network, the polymer ultimately becoming insoluble. Crosslinking is more commonly brought about by using high energy radiation. For example, this is the usual method for producing crosslinked polyethylene[32]. Whether or not crosslinking takes place when a polymer is irradiated depends to a large extent on the structure of the polymer. Polystyrene[33,34] and poly-(methyl acrylate)[35] readily crosslink on exposure to ultra-violet radiation while poly-(α-methyl styrene)[20] and poly-(methyl methacrylate)[35] only do so if sensitisers are present. The former pair of polymers have hydrogen atoms alpha to the pendant groups which are readily transferred and the resultant polymer radicals are resonance stabilised. Combination with other polymer radicals can occur resulting in branched chains and eventually a three dimensional network is built up. On the other hand, the α-methyl groups in poly-(α-methyl styrene) and poly-(methyl methacrylate) prevent formation of stabilised radicals and

chain scission rather than crosslinking takes place. When crosslinking does occur it has a considerable effect on the interpretation of photodegradation results, making molecular weight determinations impossible, although sedimentation pattern and gel fraction studies can be made. Crosslinking also interferes with the determination of the rate of evolution of since the rigid structure has a much higher bulk viscosity which slows down the rate of diffusion of small product molecules.

Photolysis of Polymethacrylates.

Early work on the photolysis of polymethacrylates was carried out by Cowley and Melville[24] who irradiated poly-(methyl methacrylate) films with 2537Å radiation. This work followed on from the thermal degradation studies of the same polymer by Grassie and Melville[25]. Cowley and Melville studied the formation of monomer during the irradiation of thin films in vacuum using a molecular still, the evolution of monomer being followed by means of a calibrated Pirani gauge. The reactions were carried out over the temperature range 170-200°C, since there was a break in the activation energy plot at about 165°C. Below this temperature the energy of

activation appeared to be approximately 12.5×10^4 J/mole. This value is almost identical to the energy of activation for the diffusion of methyl isobutyrate, which has a similar structure to monomeric methyl methacrylate, through poly-(methyl methacrylate)[37]. This would appear to confirm the authors' conclusions that the change in the activation energy is due to slower diffusion of monomer through the more viscous polymer at lower temperatures. Frolova and Riabov[38] exposed poly-(methyl methacrylate) powder and thin films to ultra-violet light in vacuum at 25°C. Gaseous products were evolved. The quantum yield for wavelength range 3030-3130Å was 2.3×10^{-4} molecules of gas evolved per quantum absorbed. By shorter wavelength irradiation of samples tagged with C^{14} it was shown that the ester groups were the primary source of these gases and that methyl formate was a major product. Shultz[39] irradiated thin films of poly-(methyl methacrylate) with 2537Å at 26°C in air. The result was almost solely chain scission with no cross-linking. This was later confirmed in work by Fox, Isaacs, Stokes and Kagarise[35] which included a study of sedimentation patterns. This absence of crosslinking is known to exist even with ionising radiation[40]. It is possible to

crosslink poly-(methyl methacrylate) using ultra-violet radiation but only in the presence of sensitisers[41]. The appearance of a broad absorption peak near 2850Å was noted in the ultra-violet absorption spectrum after irradiation.

Monig[42] irradiated poly-(methyl methacrylate) in chloroform, dioxane and benzene solutions of concentration 0.3lg./litre at 20°C. The extent of degradation was followed through changes in viscosity. The mechanism appeared to be one of random scission with no monomer production. The extent of decomposition in a given time period varied considerably with solvent indicating solvent participation in the reaction. Charlesby and Thomas[43] irradiated poly-(methyl methacrylate) in the form of thin films and benzene solutions at room temperature with both ultra-violet and gamma radiation. The results for solution irradiation showed that degradation was linear with dose and was effectively independent of polymer concentration over a twenty fold range in concentration. This indicated that the benzene did not participate in the reaction. In spite of the high absorption by the solvent there appeared to be no energy transfer to the polymer. Irradiation of films with low and medium

pressure lamps gave similar results. Film photolyses were carried out in atmospheres of air and nitrogen, the rates of chain scission being almost equal. From e.s.r. studies of the ultra-violet and gamma irradiated polymer it was concluded that there was random initiation but that this was not followed by depropagation. This differed considerably from high temperature results such as those of Cowley and Melville but differences due to temperature were also found in the results from high energy irradiation. High energy irradiation at room temperature leads to random scission and no depropagation and therefore no monomer whereas at higher temperatures random scission occurs accompanied by depropagation and liberation of monomer. Later investigations by Charlesby and Moore[44] at temperatures up to 180°C confirmed many of the similarities between degradation by ionising and ultra-violet radiation.

Maxim and Kuist[45] compared rate of chain scission by ultra-violet and high energy radiation of poly-(ethyl methacrylate) and poly-(methyl methacrylate). They noted that the energy of radiation of ultra-violet radiation is of the same order of magnitude as chemical

bonds. This is why ultra-violet radiation is bond selective and why its effects can vary with wavelength, unlike high energy radiation.

Kardash and Krongauz[46] irradiated solutions of poly-(methyl methacrylate)in benzene with 2537Å light. plots of polymer concentration versus quantum yield reached a constant value at 3.2×10^{-6} scissions/quantum. It was concluded therefore that the polymer is not decomposed by the light directly. The addition of free radical acceptors almost completely stopped the degradation. The results were interpreted as showing that irradiation probably induces the formation of benzene free radicals which then react with the polymer.

Fox and Price[47] irradiated poly-(methyl methacrylate) (5g./litre) in methylene chloride and other solvents at room temperature. The quantum yields for random scission were independent of polymer concentration but dependent on the solvent used. Therefore it was concluded that they should be evaluated on the basis of energy absorbed only by the polymer i.e. after the effect of optical filtering by other constituents of the solution had been taken into account. Calculated in this manner the rates of chain

scission were found to be identical for methylene chloride and dioxane solutions. Oxygen was found to act as an inhibitor. It was concluded that solvent radical attack may not be as important as other means of transferring energy to and from the polymer. These authors also studied the effect of small amounts of a variety of additives on the quantum yields for scission of poly-(methyl methacrylate) in the above solvents at room temperature in the presence and absence of air.[18,47,48] For degassed solutions, quantum yields for random scission based on energy absorbed by the polymer were little affected by either intensity or polymer concentration. The effects of added solutes whether or not oxygen was present. The authors were able to show a correlation between the degree of inhibition or acceleration of degradation and the lowest excited triplet energy levels of the additives. This was interpreted to indicate the existence of an electronic transfer mechanism and that poly-(methyl methacrylate) may undergo photodegradation from an excited triplet state.

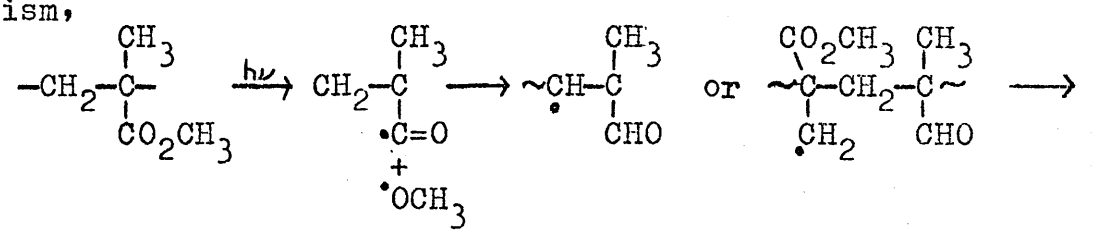
Somewhat similar studies of "indirect" photodegradation were carried out by Monig and Kriegel[49-51] who investigated the sensitising effect of polycyclic aromatic

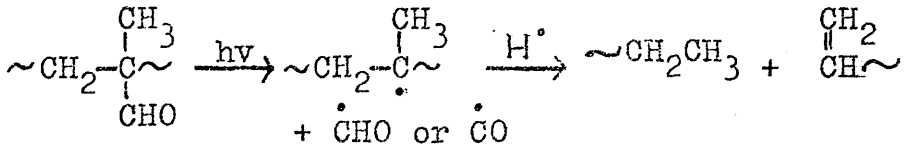
hydrocarbons on the photolysis of poly-(methyl methacrylate) in solution. Radiation that was absorbed by the additives but not by the polymer was used. The mechanism of sensitisation probably involves an oxygen-transfer reaction which involves both the solvent and the photolysis products from the polycyclic hydrocarbon.

Jellinek and Wang[52] made a kinetic study of the 2537Å photolysis of poly-(methyl methacrylate) in solutions of 2-chloroethanol under nitrogen at 25°C and 159°C. The extent to which oxygen was present in these solutions was not known. The experimental rate constants were dependent on polymer concentration which indicated participation of the solvent in the photolysis reaction. Thermal degradation was negligible even at 159°C. The intensity exponent and activation energy for monomer production were very similar to the results of high temperature bulk degradation studies by Cowley and Melville[24]. The kinetic picture differed from that of Cowley and Melville in that even at elevated temperatures random initiation was indicated. The kinetics of the process satisfactorily fit a sequence of direct random photolysis of the polymer and random chain scission caused by the

solvent radicals followed by monomer formation and a diffusion controlled second order termination. It should be noted that repolymerisation may also occur since the monomer produced remains in solution and therefore in the vicinity of a significant concentration of polymer radicals.

Allison[53] irradiated methyl methacrylate copolymers at 30°C in vacuum. Aldehydes were chosen as comonomers since their participation in the chain scission reaction was suspected[19]. The polymers were irradiated in the form of expanded films produced by a freeze-drying technique. During degradation at least one molecule of carbon monoxide was evolved for each chain scission. Other products were methyl formate and methanol. The ultra-violet absorption near 2850Å previously noted by other investigators was tentatively assigned to aldehyde groups formed as a result of irradiation. It was concluded that chain scission of poly-(methyl methacrylate) was primarily the result of these photo-induced aldehyde groups. The following was proposed as a possible mechanism,





Fox, Isaacs, Stokes and Kagarise[35] studied the photolysis of thin films of poly-(methyl acrylate) by 2537Å radiation at 22°C in vacuum and in air. No skin effect was observed. Insoluble crosslinked material was found early in the vacuum runs and qualitative comparison of the sedimentation patterns of degradaded and undegraded polymer indicated that crosslinking occurred in both air and vacuum. Oxygen must act to reduce crosslinking since no benzene insoluble material was obtained in air photolysis. Spectral changes were minimal with the formation of a weak band at about 2800Å in the ultra-violet spectrum. No evolution of monomer was detected.

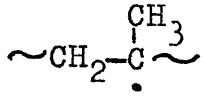
Photolysis of Copolymers of Methyl Methacrylate and Methyl Acrylate.

The photolysis of copolymers of methyl methacrylate (MMA) and methyl acrylate (MA) was studied at 170°C in vacuum by Grassie, Torrance and Colford[54] using 2537Å radiation. From molecular weight measurements of the degraded polymers, it was concluded that a random scission

process occurs. No insoluble material was observed even in the photodegraded 2/1 MMA/MA copolymer. From analysis of the volatile products it was found that one in ten of the methyl acrylate units was liberated as monomer compared with one in four in the purely thermal reaction.[55] The zip length for depolymerisation of the photo reaction was found to be very much greater than in the thermal reaction and since the zip lengths decreased with increasing methyl acrylate content it was deduced that the methyl acrylate units must block the depropagation reaction. This blocking is not complete however since small amounts of monomeric methyl acrylate appear in the volatile products. The rate of chain scission was not found to be strongly dependent on the methyl acrylate content showing that scission occurred at random points along the chain and not preferentially at methyl acrylate units. Recently, Grassie and Scotney[56] have been studying the photolysis of methyl methacrylate/methyl acrylate copolymer films at room temperature using 2537Å radiation. Their results are discussed in chapter 5.

Aim of this Work.

Although a great deal of effort has been concentrated on the photodegradation of homopolymers, very little has been directed at the study of copolymer degradation. Degradation reactions occurring in copolymers are particularly interesting because they demonstrate how two monomers with different degradation characteristics interact when they are found in the same polymer molecule. Polymethacrylates and polyacrylates are very similar structurally but many of their degradation characteristics are quite different. Under ultra-violet radiation at room temperature, poly-(methyl methacrylate) films undergo chain scission with a corresponding rapid drop in molecular weight while poly-(methyl acrylate) rapidly becomes insoluble due to crosslinking. However, the gaseous products of photolysis of both polymers are identical[57] and thus it seems clear that in both polymers, volatile products are a result of decomposition of the ester side group following its scission from the polymer chain. The reactions of the resulting polymer radical ;



determine the more obvious changes which occur. The

polymethacrylate radicals predominantly undergo chain scission whereas acrylate radicals mainly combine to form crosslinks.

The study of polymer degradation reactions in the solution phase has received relatively little attention. The use of solutions in polymer photolysis affords some freedom to study the interaction between polymer and other molecules since the composition of the solution can be accurately controlled and is uniform throughout. In addition, problems due to bulk polymer properties, for example, solid phase transitions and small molecule diffusion through a solid polymer, will be eliminated in solution work. The probability of crosslinking should be decreased through the separation of the polymer chains by molecules of solvent unless perhaps the polymer chains are agglomerated in a micelle.

In these laboratories a great deal of work on the photolysis of homopolymers and copolymers is being carried out in an attempt to contribute to the fundamental understanding of photodegradation processes. This work involves the photolysis of polymer films; the comparison of reactions occurring in copolymers with those which are characteristic of the homopolymers; the study of the

effect of crystallinity on the rate of degradation; the relative rates of degradation above and below the glass transition temperature; the influence of radiation on subsequent thermal properties of the polymer and comparison of the photolysis reactions which occur in molten polymers (photo-thermal degradation) with the purely thermal reaction which occurs at slightly higher temperatures. As part of this programme, it was considered desirable to compare the photodegradation characteristics of the polymers in film form with those occurring in solution.

CHAPTER 2.

EXPERIMENTAL TECHNIQUES AND APPARATUS.

2.1. Preparation of Copolymer Samples.

a. Purification of Monomers.

Methyl methacrylate, methyl acrylate and methacrylonitrile.

Methyl methacrylate [B.D.H. Ltd.], methyl acrylate [B.D.H. Ltd.] and methacrylonitrile [Eastman Kodak Co.] were washed three times with 5M sodium hydroxide to remove the hydroquinone inhibitor, followed by three times with distilled water to remove traces of alkali. The purified monomers were dried for 24 hours over anhydrous calcium chloride followed by 24 hours over freshly dried calcium hydride. Finally, the monomers were filtered into reservoirs containing some calcium hydride and stored in the dark, in a refrigerator at -18°C until required.

Before use the monomers were degassed twice in a reservoir attached to a high vacuum apparatus consisting of an Edwards silicone oil vapour diffusion pump backed by an Edwards rotary oil pump. Degassing was effected by the usual cycles of freezing with liquid nitrogen, pumping off released dissolved gases and thawing. The first ten per cent of each monomer was distilled off and discarded after which the quantity required was distilled

into a graduated reservoir and finally into the polymerisation dilatometer.

Styrene.

Styrene [Forth Chemicals Ltd.] contained 0.1% p-tert-butylcatechol as inhibitor. This was removed and the monomer purified by a procedure similar to that described above.

Maleic anhydride.

Maleic anhydride[B.D.H. Ltd.] was purified by distillation under atmospheric pressure [M.Pt. 53°C, B.Pt. 199°C-202°C] and stored in a dark container until required.

b. Purification of Initiator.

In all polymerisations described in this work, the initiator used was 2,2′ azo-bisisobutyronitrile which was purified by recrystallisation from Analar methanol [M.Pt 104° C]. The initiator was introduced into the polymerisation dilatometers as a freshly prepared solution in Analar toluene, the solvent being partially removed by a water pump then completely removed by pumping for about an hour on the high vacuum apparatus, light being excluded to prevent decomposition of the initiator.

c. Preparation of polymerisation dilatometers.

i. The dilatometers.

Pyrex glass dilatometers of approximately 100ml.

capacity with a 5ml. graduated stem were washed overnight with cleansing solution, distilled water and finally Analar acetone and attached to the vacuum apparatus. The dilatometers were then flamed intermittently for about an hour prior to the addition of the initiator solution.

ii. Addition of monomers.

Monomer mixtures of pre-determined composition were distilled under vacuum into the dilatometers and finally degassed before sealing off at a pressure of less than 10^{-5} torr.

In the case of maleic anhydride, the monomer was ground to a fine powder and the required weight added directly to the dilatometer which was then placed on the vacuum line and pumped for several hours before addition of the other monomer.

d. Polymerisation

All polymerisations, except that of methyl acrylate homopolymer, were carried out in bulk in a thermostatically controlled water bath at $60 \pm 0.5^{\circ}C$. Methyl acrylate was polymerised in solution using Analar methyl acetate as solvent. In addition to the copolymers covering the whole composition range, homopolymers of methyl methacrylate, methyl acrylate, styrene and methacrylonitrile were prepared so that it was possible to study the degradative

characteristics of the entire composition ranges of these systems.

The progress of the polymerisations were followed dilatometrically and stopped at approximately 8% by immersing the dilatometer bulb in a freezing mixture.

e. Calculation of monomer feed composition.

The molar ratios of monomers necessary to produce copolymers of the required composition were calculated using the copolymer composition equation;[58,59,60,61].

$$\frac{P_1}{P_2} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{M_1 + r_2 M_2}$$

where P_1 / P_2 is the ratio of the molar concentrations of the two monomers in the copolymer and M_1 / M_2 is the ratio of the molar concentrations of the monomers in the feed. This relationship applies if the conversion to the polymer is sufficiently low for the monomer concentrations to remain unchanged; r_1 and r_2 are the reactivity ratios of the two monomers M_1 and M_2 respectively and the values used in this work are shown in table 2.1.

f. Polymer recovery.

Polymerisation reactions were stopped by immersing the dilatometer bulb in a freezing mixture, the dilatometer broken, the contents dissolved in the appropriate solvent as indicated in table 2.2. and the polymer

precipitated by slow dropwise addition of the solution to 4 litres of Analar methanol with constant stirring. After decantation of the supernatant liquid, the polymers were partially dried under vacuum at room temperature. The polymers were reprecipated twice more from solution in this manner.

g. Polymer purification.

1. Homopolymers and copolymers of methyl methacrylate and methyl acrylate.

Those copolymers with a high methacrylate content precipitated as finely divided powders while acrylate rich samples were more coagulated and rubbery and were thus difficult to dry completely. Because of this, all of the acrylate/methacrylate copolymers were freeze dried from solution in Analar benzene to remove all traces of solvent.

2. Copolymers of methyl methacrylate with styrene, maleic anhydride, and methacrylonitrile.

These copolymers gave flocculent precipitates which after decantation of the supernatant liquid, were partially dried as before, then ground to a finely divided powder and dried in a vacuum oven at 50°C for several days.

2.2. Photolysis of Polymers.

a. Photolysis apparatus.

Photochemical reactions must be carried out in a

vessel made of silica which is transparent to the ultra-violet radiation used. The types of photolysis cells used in this work are shown in figs.(1,2,3,4.) and the disposition of the cells to the radiation source is shown in figs.(5,6,7.) The apparatus in fig.5 consists of an ultra violet lamp with a fixed wooden screen,containing 4 holes, clamped in a position parallel to the light source. The 5 cardboard partitions shown give separate irradiation positions enabling 4 degradations to be carried out at the same time.

Fig.7 shows the apparatus used when stirring of the polymer solutions was required, the irradiation in this case being effected from above.

b.Preparation and photodegradation of polymer solutions.

Exactly 1g. of polymer was weighed out and dissolved in 50ml. of the pure, dry solvent chosen for irradiation. A graduated syringe was used to transfer 4ml. of polymer solution to the silica irradiation cell. Four identical cells were used at any one time, the solution in each cell being degassed four times on the vacuum line, as described previously, by freezing and thawing cycles in liquid nitrogen. This technique removes all dissolved gases, in particular oxygen, which might inhibit or accelerate the photodegradation.

The cells were sealed off under a pressure of less than 10^{-5} torr, removed from the vacuum system and clamped in the positions shown in figs.(5,7.). Fig.5 shows the flat bottomed silica cells clamped such that they are flush with the fixed wooden screen, ensuring that they are always the same distance from the source of irradiation.

During irradiation, the apparatus was screened by cardboard sheets to minimise the harmful effects of the ultra-violet light.

The cells shown in fig.5 were removed individually after specific periods of time and in this way irradiations of up to several hours were carried out. On the apparatus shown in fig.7 however, only one irradiation could be carried out at a time due to the bulk of the magnetic stirrer used.

c. Recovery of polymer.

After irradiation each cell was broken open at positions X and Y shown in figs.(5,7.) and the contents transferred to a clean dry open-necked bottle using a few ml. of the solvent used for degradation to ensure that as much polymer is recovered as possible. The open-necked bottle was then placed in a water bath at about 70°C and the

solvent removed by blowing filtered air on the surface of the solution as shown in fig.8. The heated water bath prevents excessive cooling of the solution caused by the removal of latent heat of evaporation and speeds solvent removal. When most of the solvent had been removed the bottle was transferred to a vacuum line and the remaining solvent removed under vacuum as shown in fig.9. The bottle and the solid polymer contents were then transferred to a vacuum oven at 60°C, left overnight and subsequently cooled and weighed. Usually, a polymer recovery yield of at least 95% was obtained.

d. Preparation of polymer solutions for molecular weight analysis.

Once all of the solvent had been removed from the photodegraded polymer sample, the approximate weight of the sample was obtained(2.2.c.) and sufficient Analar toluene or cyclohexanone added to give a solution of 1% W/V for molecular weight analysis. The exact concentrations were determined by evaporating 1ml. portions ofthe solution to constant weight in a pre-weighed bottle. Evaporation was carried out in the vacuum at 100°C, usually for about 3 hours.

2.3. Photo-oxidation of methyl methacrylate/methyl acrylate copolymers.

a. Preparation of polymer films.

Solutions of the polymers in Analar methyl acetate as solvent were prepared accurately to a concentration of 30mg. per ml. Two ml. of the solution were pipetted on to a polished silica disc, diameter 25mm., thickness 1mm. and the solvent allowed to evaporate slowly. Once the methyl acetate had evaporated, leaving a film of polymer, the disc was transferred to the vacuum oven and evacuated overnight at 60°C to remove all residual solvent.

b. Preparation of photolysis cell.

The photolysis cell used is shown in fig. 4. The polymer film plus disc was placed in the cell as shown and the cell was completely evacuated on the vacuum system. Oxygen gas was then introduced to the system to a pressure of 150mm. Hg., the pressure being monitored by a mercury manometer. Taps C and D were closed and the cell was left on the vacuum system overnight to ensure complete diffusion of the oxygen into the polymer films. Any change in the oxygen pressure due to diffusion of the gas into the polymer films would be negligible when taken over the large volume of the system. Tap A

was then closed, the cell removed and clamped above the radiation source.

Irradiations of up to 4 hours were carried out. The film was separated from the disc by immersion in distilled water. After a few minutes it was possible to peel off the film from the disc and after drying in the vacuum oven at 60°C it was weighed before submitting it to molecular weight and spectroscopic analyses.

c. Preparation of solutions.

4ml. of solutions of concentration 20mg. per ml. were transferred by syringe to the photolysis cell shown in fig.2. The solutions were degassed as previously before addition of 150mm. Hg pressure of oxygen gas then sealed off using the Teflon stopcock Y. The cell was then clamped in position above the irradiation source as in fig. 5. and the contents were irradiated for periods of up to 2 hours. The polymers were recovered as in section 2.2.c. and submitted for molecular weight analysis.

2.4. Photolysis of polystyrene.

a. Solutions of polystyrene.

Solutions of concentration 20mg. per ml. of polystyrene were prepared with Analar chloroform,

methylene chloride, dichloroethane, methyl acetate and cyclohexane as solvents. These were irradiated in cells of the type shown in fig.3. for periods of up to 12 hours duration. Ultra-violet and infra-red spectra of the irradiated polymer were recorded.

b. Thin films.

These were prepared from solutions of concentration 10mg. per ml. in Analar chloroform. Two ml. portions were pipetted on to polished silica discs and the solvent allowed to evaporate slowly. The polymer film formed was dried in the vacuum oven at 60°C, placed in the photolysis cell fig.4., which was evacuated on the vacuum system before closing the stopcock. The films were then irradiated for periods up to 10 hours and the U.V. and I.R. spectra recorded.

c. Complete removal of solvent.

Since the previous method of removing all residual chloroform from the polystyrene films was found to be unsatisfactory, an alternative method was tried. This involved heating the 20mg. polystyrene film plus silica disc under vacuum using a heating bath of silicone oil at 180°C, the rate of solvent removal being monitored with a Pirani gauge head attached to the vacuum system

as shown in fig.10. When the Pirani gauge registered zero pressure, the molten film was allowed to cool slowly, the photolysis cell closed at tap X and the cell clamped above the radiation source. Control runs were carried out whereby the polystyrene films after this treatment were subjected to Thermal Volatilisation Analysis, the thermograms obtained were compared with those obtained from analysis of polystyrene films purified by the previous method.

2.5. Molecular weight measurement.

a. Introduction.

The study of molecular weight changes which occur during the degradation of polymers and copolymers must normally form an important part of any investigation of this type. The osmotic pressure method, which yields number average molecular weights has been particularly valuable in degradation investigations. This method has been extensively reviewed by Hookway[66]. The swift attainment of equilibrium in modern osmometers greatly reduces the problem of diffusion which was troublesome in the earlier use of this technique.

The basic equation relating osmotic pressure to number average molecular weight $\bar{M}n$ is the expression

of van't Hoff;

$\pi = RTC/\overline{M}n$ where R and T have the usual significance. The molecular weight is obtained by measuring the osmotic pressure of solutions of the polymers of different concentrations and by plotting π/C versus C.

π = osmotic pressure

C = concentration of polymer g/100g.

this leads to a straight line plot from which $(\pi/C)_o$ may be obtained by extrapolation to infinite dilution. A simple conversion factor[67] of $2.53 \times 10^5 / (\pi/C)_o$ gives the number average molecular weight directly from $(\pi/C)_o$. A typical plot of osmometer data is shown in fig.12.

b. Mechrolab High Speed Membrane Osmometer.

The Mechrolab 501 High Speed Osmometer[68] was used throughout this investigation with Cellophane 300 membranes. Analar toluene was used as solvent except in the case of copolymers containing methacrylonitrile when cyclohexanone was used due to the insolubility of these copolymers in toluene. The osmometer was thermostatted at 25°C and solutions of concentrations 0.5g. to 1g. per

100g. solvent were used.

c. Treatment of molecular weight determinations.

If a polymer is subjected to some degradative influence such as ultra-violet irradiation, its molecular weight may or may not alter. If the molecular weight decreases due to chain scission, the number of scissions per polymer molecule may be calculated. If N is the number of chain scissions which have occurred per polymer molecule and CL_o and CL are the chain lengths at zero time and after N breaks respectively then, provided that no volatilisation of the polymer results,

$$N = [CL_o/CL] - 1 \quad \text{- - - - - - - - - - - - (1)}$$

For the purpose of comparison of polymers and copolymers of different molecular weights, it is more convenient to express the number of chain scissions in terms of scissions per monomer unit rather than per polymer molecule. Thus if n is the number of chain scissions per monomer unit

$$N = nCL_o \quad \text{- - - - - - - - - - - - (2)}$$

and

$$n = 1/CL - 1/CL_o \quad \text{- - - - - - - - - - - - (3)}$$

2.6. Source of Radiation - The ultra-violet lamps.

a. Introduction.

The need to use short wavelength ultra-violet radiation (2537Å) has already been discussed and a Hanovia Chromatolite Lamp was used. In order to investigate the effect of longer wave ultra-violet radiation on the reaction however, a Hanovia Fluorescence Lamp model 11 was used. The lamps were connected to an L.T.H. Transistorised 1kVA Voltage Regulator to ensure that any variations in the mains output did not affect the lamp emission.

b. Output of Hanovia Chromatolite Lamp.

This lamp employs a low pressure mercury arc to produce a typical mercury spectrum, the intensity of the two resonance lines at 1849Å and 2537Å being much greater than those of all the other wavelengths present. The output of this lamp is shown in fig.13. The photolysis cells were placed above and below the discharge tube as as shown in figs.5 and 7.

c. Hanovia Fluorescence Lamp Model 11.

The ultra-violet radiation from this lamp is provided by a high pressure mercury arc. The arc is produced tungsten electrodes in a silica tube. The U.V. radiation is distributed over the characteristic lines of the

mercury spectrum as shown in fig.14. A filter of Wood's glass is incorporated in the lamp and this effectively absorbs all but the most powerful band of radiation around 3660Å.

2.7. Transmission of Ultra-Violet Radiation.

a. Introduction.

The output of the lamp traversed at least 10cm. of air and 2mm. of silica before finally entering the polymer samples to be irradiated. The nature of the radiation eventually reaching the solutions is modified to some extent by the absorption characteristics of these media and it is therefore worthwhile to examine these characteristics.

b. Transmission by air.

An examination of the composition of air reveals that the only component which is capable of absorbing the ultra-violet radiation produced by these sources is oxygen, the other constituents being completely transparent in this region of the spectrum. The oxygen absorption spectrum consists of two sets of bands, the one system converging at 2400Å and the more important Schumann-Runge system having a threshhold wavelength at 2000Å and converging towards[69,70] 1761Å. Corresponding

to these two absorptions are the two photo-dissociations of oxygen molecules,

$$O_2 + h\nu \longrightarrow O(^3P) + O(^1D)$$

and $$O_2 + h\nu \longrightarrow 2O(^3P)$$ respectively.

Ozone is produced concurrently according to the equations,

$$O(^1D) + O_2 + M \longrightarrow O_3 + M$$

$$O(^3P) + O_2 + M \longrightarrow O_3 + M$$

where M is the necessary third body.

It is obvious then that only the 1849Å line has an energy associated with it which exceeds the threshhold energy for the photo-dissociation of oxygen. This line is therefore absorbed by the air and a path length of only 1cm. in air is sufficient to absorb it completely.[71]

c. Water vapour.

The absorption spectrum of water, 1cm. is shown in fig.15. With the exception of 1849Å radiation the water vapour in the air between the discharge tube and the cell will be transparentto all wavelengths.

d. Fused silica.

The transmission of fused silica is shown in fig.16. and is seen to be transparent to the wavelengths used for photolysis.

e. Monochromaticity of the source.

It has been shown that 93% of the lamp is composed of the mercury resonance radiation with wavelengths of 1849Å and 2537Å and that in passing from the arc to the polymer, the intensity of the former is reduced to an extremely low value. The intensity of the latter is only slightly attenuated. This means then that since the intensities of the longer wavelength radiations are negligible compared with that of the 2537Å, the radiation reaching the polymer is virtually monochromatic.

2.8. Determination of the Absolute Numbers of Quanta Produced by the Lamp.

a. Introduction.

In order that the results of photolysis may be treated in a quantitative manner and that the results emanating from a particular radiation source may be compared quantitatively with those from another, it is necessary to know the absolute number of quanta produced by the lamp. The method used in this work was that using the potassium ferrioxalate solution phase chemical actinometer developed by Hatchard and Parker[5], which is simple to use and very sensitive over a wide range of wavelengths. It is based on the fact that when sulphuric acid solutions

of $K_3Fe(C_2O_4)_3$ are irradiated with light of wavelengths 2500-5770Å, the iron is reduced to the ferrous state and the oxalate is oxidised. After irradiation, the ferrous iron can be converted into the red-coloured 1,10 Phenanthroline Fe^{2+} complex which is highly absorbing and easily analysable.

b. Experimental procedure.

Solid green crystals of $K_3Fe(C_2O_4)_3$ were prepared as described by Hatchard and Parker[5] and Calvert and Pitts[2] the latter giving a fully detailed summary of the procedure. All manipulations and preparations of the ferrioxalate solutions were carried out in a dark room. A standard calibration graph for the analysis of the Fe^{2+} complex was drawn as in fig.17. using a Hitachi Perkin Elmer 139 Ultra-violet Spectrophotometer.

The light intensity in the photolysis cell was determined by irradiating 15ml. of ferrioxalate solution (V_1) in a current of oxygen free nitrogen gas for a period of 60 seconds. After mixing the solution, 10ml.(V_2) was pipetted into a 25ml. volumetric flask (V_3) and the phenanthroline complex prepared, along with an identical blank solution in the reference beam.

The number of Fe^{2+} ions formed during the photolysis

(nFe^{2+}) was calculated using the formula;

$$nFe^{2+} = \frac{6.023 \times 10^{20} V_1 V_2 \log I_o/I}{V_2 LE} \qquad \text{A.}$$

where V_1= Volume of actinometer solution irradiated(ml.)

V_2= Volume of aliquot taken for analysis (ml.)

V_3= Final volume to which aliquot V_2 is diluted(ml.)

$\log I_o/I$ = measured optical density of the solution at 5100Å (the "difference" O.D. between the unexposed and irradiated solutions.)

L = the path length of the spectrophotometer cell used(cm.).

E = the experimental value of the molar extinction coefficient of the Fe^{2+} complex as determined from the slope of the calibration graph.

The average "difference" optical density = 0.229

∴ from equation A, the number of Fe^{2+} ions formed

$= 4.382 \times 10^{17}$.

The intensity of the light beam incident, I_o^i was calculated from[2]

$$I_o^i = nFe^{2+} / \Phi_{Fe^{2+}} t[1-10^{-E(A)S}] \text{ quanta/sec.----B.}$$

where $\Phi_{Fe^{2+}}$ is the quantum yield of the product Fe^{2+} this being accurately known for radiation of 2537Å, $I_{Fe^{2+}}$=1.25.

t = time of exposure.

$(1-I/I_o) = (1-10^{-EAS})$ = fraction of incident light absorbed. Using equation B,

$I_o^i = 5.68 \times 10^{15}$ quanta / sec.

Therefore the intensity of the light beam impinging on the photolysis cells = 5.68×10^{15} quanta / sec.

2.9. Analytical Techniques.

1. Infra-red Spectroscopy.

Infra-red absorption spectra of all polymers irradiated in solution were recorded using thin films of the polymer cast on a salt plate from a solution of the polymer in its photolysis solvent. The instrument used was an Infra-red, Grating Perkin-Elmer Model 257 Spectrophotometer. Spectra of the polymers irradiated in film form were recorded using the polymer film clamped between two brass rings which held the film rigid.

For recordings of spectra of maleic anhydride/ methyl methacrylate copolymers and succinic anhydride/ methyl methacrylate mixtures for the purpose of determining copolymer composition data, the sample form used was approximately 2mg. of polymer and 300mg. of KBr which were ground together to form a fine powder then pressed to form a rigid disc on which the spectra were recorded.

The instrument used was a PYE Unicam S.P.1000 Grating Infra-red Spectrophotometer.

2. Ultra-violet Spectroscopy.

Ultra-violet spectra were determined using a PYE Unicam S.P. Spectrophotometer. Solutions of the polymer in its photolysis solvent were used and where a study of polymer films was involved, the spectra were obtained using the polymer film cast on to a 1mm. silica disc as used in the photolysis reaction.

2.10. Copolymer Composition Analysis.

a. Introduction.

Since the investigations of this work concern the comparison of degradation characteristics of the homopolymers and copolymers covering entire composition ranges it was vital to determine the composition of the copolymers prepared in case they were significantly different from those predicted by the theoretical considerations mentioned in 2.1.c. Several methods were employed to achieve this:

a. Elemental Microanalysis.

b. Nuclear Magnetic Resonance Spectroscopy.

c. Infra-red Spectroscopy.

a. Elemental Microanalysis.

This method is especially valuable in evaluating the copolymer composition where one of the monomers contains a unique atom (eg. nitrogen chlorine or oxygen) and was applied in this work to determinations of the compositions of copolymers of methyl methacrylate and styrene where oxygen is unique to the methyl methacrylate monomer, and of methyl methacrylate/methacrylonitrile copolymers where nitrogen is unique to the methacrylonitrile monomer. The instrument used for these determinations was a Perkin-Elmer 240 Elemental Analyser, 1mg. of polymer being sufficient for accurate analysis on this instrument.

b. Nuclear Magnetic Resonance Spectroscopy.

Copolymer analysis by n.m.r. spectroscopy has been used successfully by Grassie[62.] to determine the reactivity ratios of monomers in copolymer systems in which elemental analysis was not sufficiently accurate due to similarities in the empirical formulae of the monomers and in which the copolymer molar ratio did not exceed 10/1.

Copolymer composition data for the methyl methacrylate/methyl acrylate system were obtained from n.m.r.

spectra recorded on a Perkin-Elmer R.10. 60 Mc/s. Spectrometer with an integrator using 20mg. of copolymer samples dissolved in 1ml. of deuterated chloroform. Ten integrals were obtained for each sample and the average used for the calculation of the copolymer compositions.

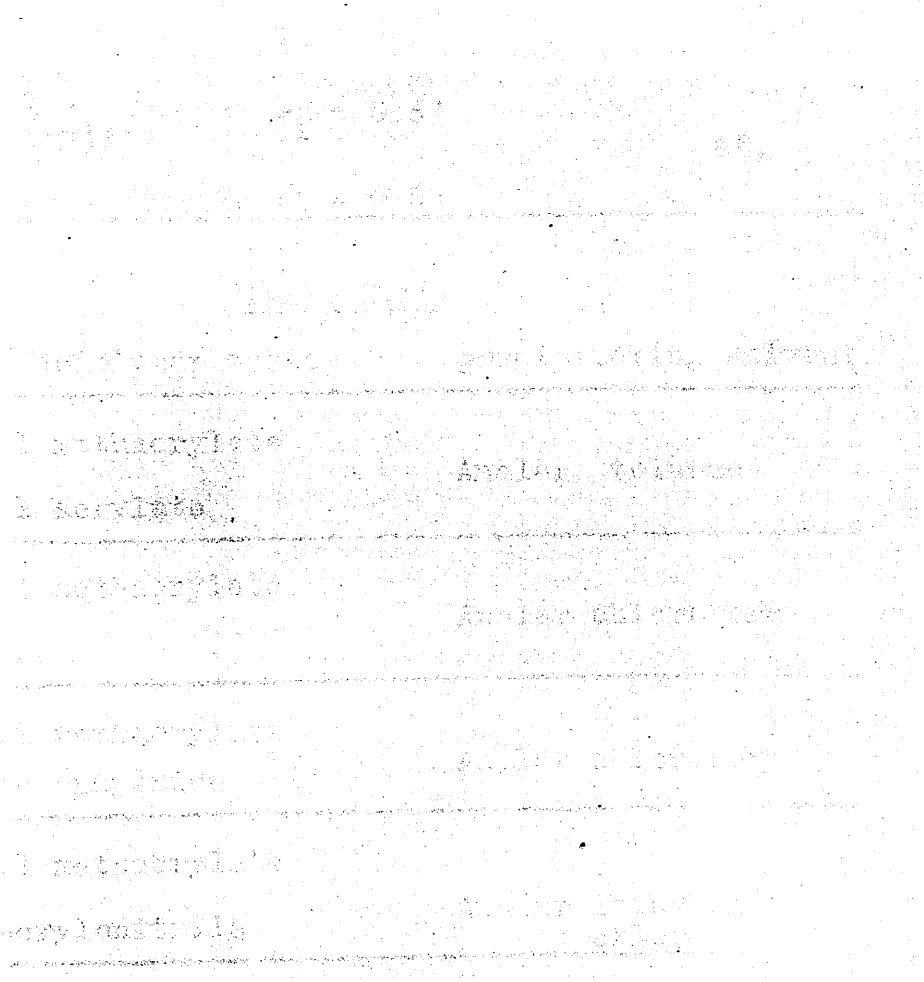


Table 2.i.

comonomers.	reactivity ratios.	reference.
methyl methacrylate methyl acrylate	$r_1 = 1.8$ $r_2 = 0.35$	62.
methyl methacrylate styrene	$r_1 = 0.46$ $r_2 = 0.52$	63.
methyl methacrylate maleic anhydride	$r_1 = 3.5$ $r_2 = 0.03$	64.
methyl methacrylate methacrylonitrile	$r_1 = 0.67$ $r_2 = 0.65$	65.

Table 2.ii.

copolymer system	precipitating solvent
methyl methacrylate methyl acrylate	Analar toluene
methyl methacrylate styrene	Analar chloroform
methyl methacrylate maleic anhydride	Analar chloroform
methyl methacrylate methacrylonitrile	Analar methylene chloride

Fig.i.

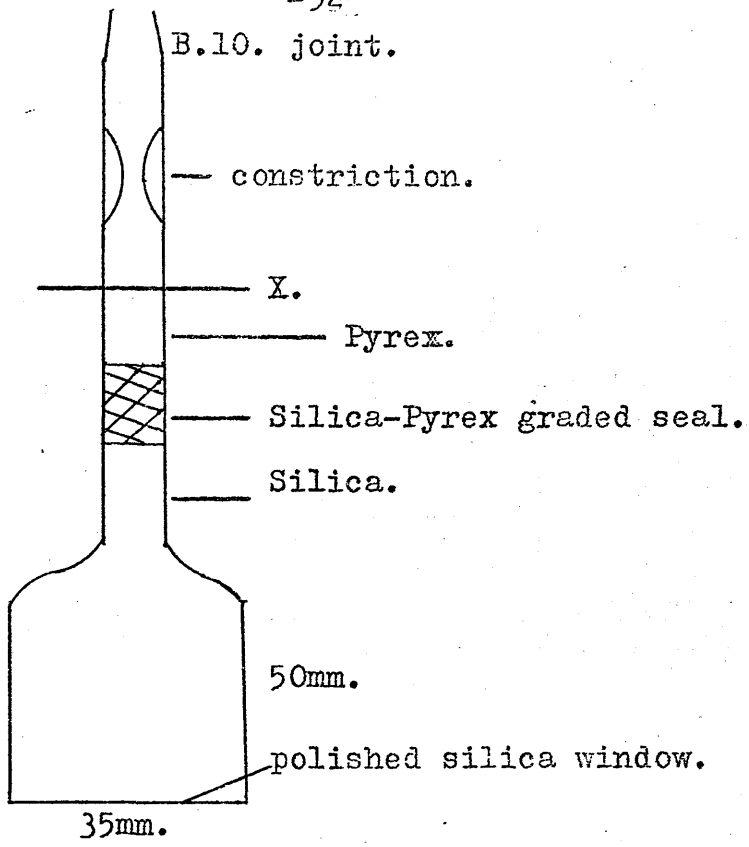

B.10. joint.
constriction.
X.
Pyrex.
Silica-Pyrex graded seal.
Silica.
50mm.
polished silica window.
35mm.

Fig.ii.

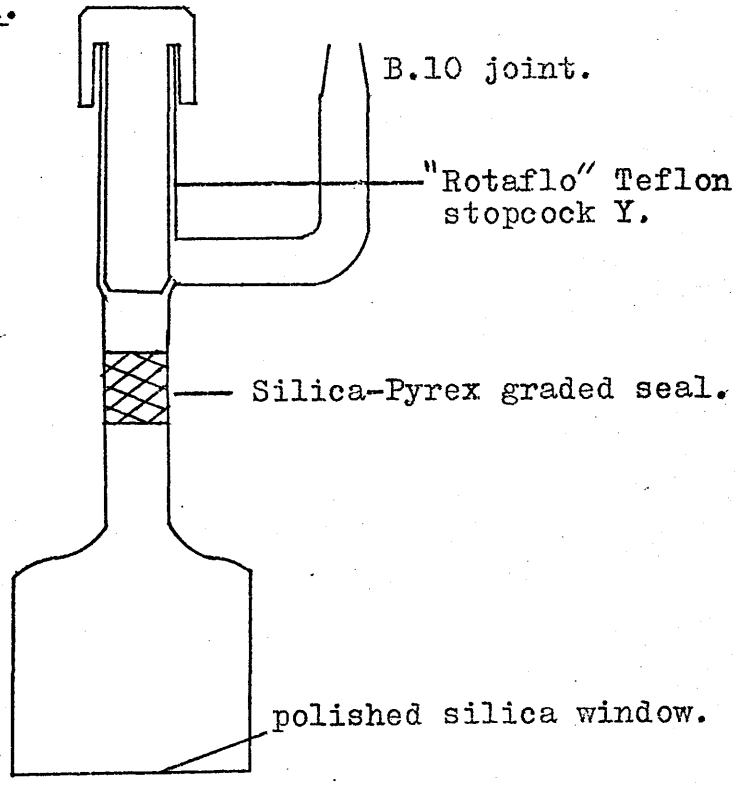

B.10 joint.
"Rotaflo" Teflon stopcock Y.
Silica-Pyrex graded seal.
polished silica window.

Fig.iii.

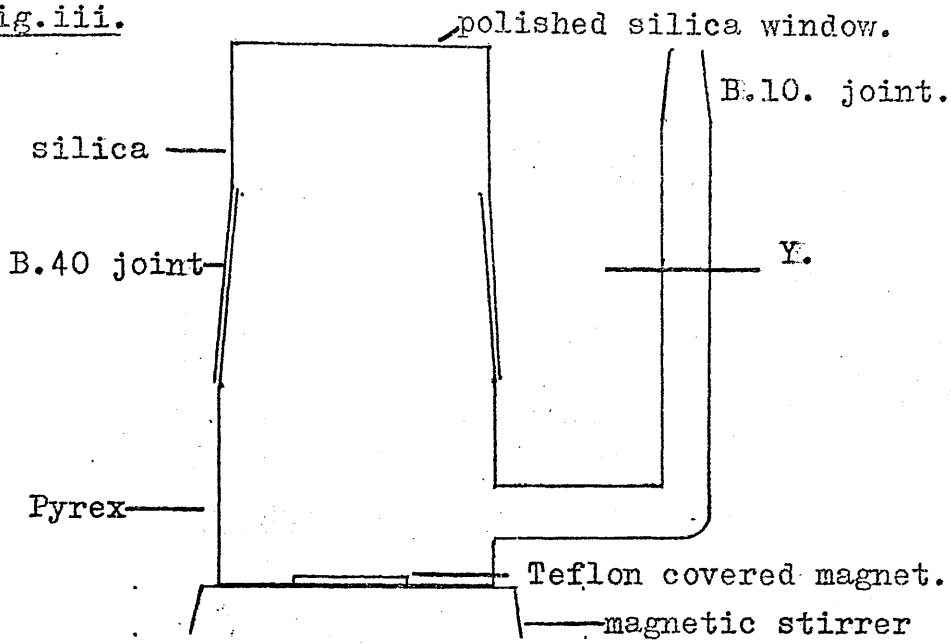


Fig.iv.

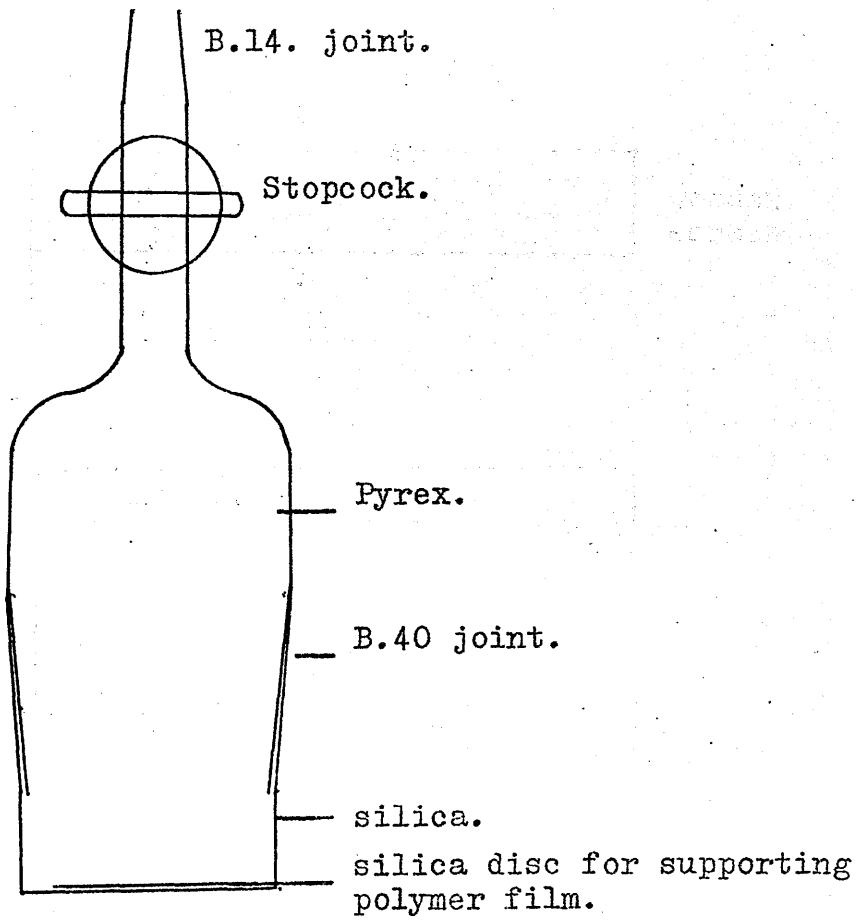
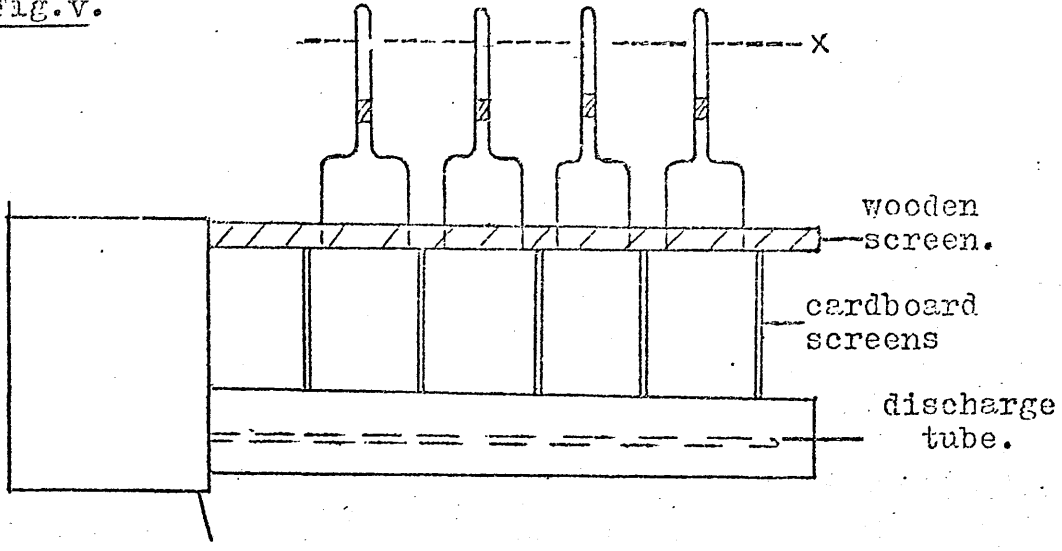
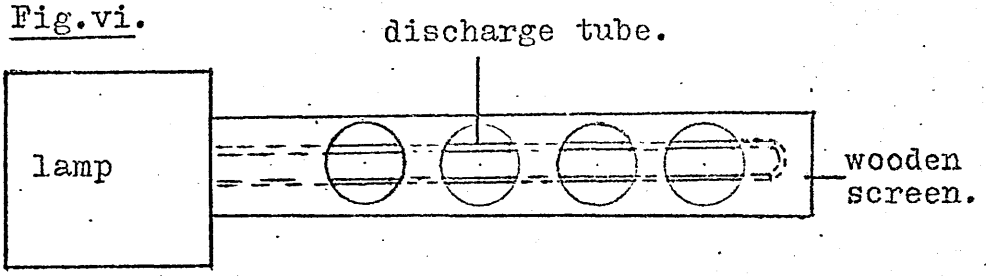


Fig.v.



U.V. Hanovia Chromatolite Lamp.

Fig.vi.



top view.

Fig.vii.

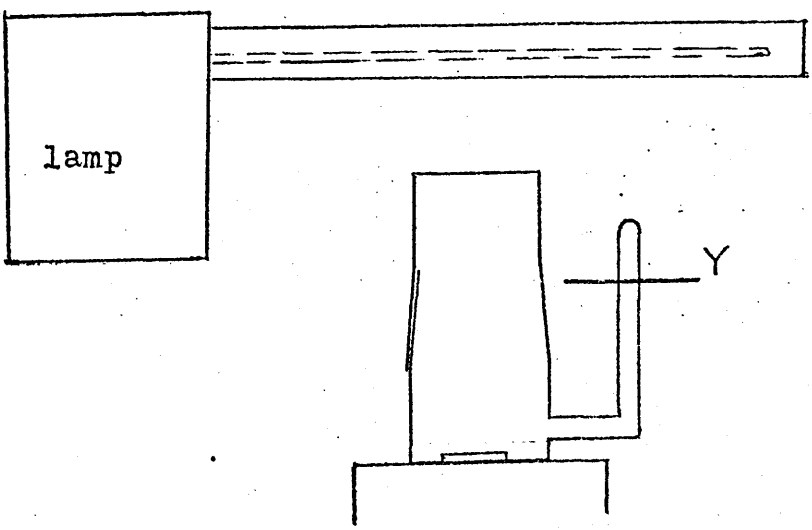


Fig.viii.

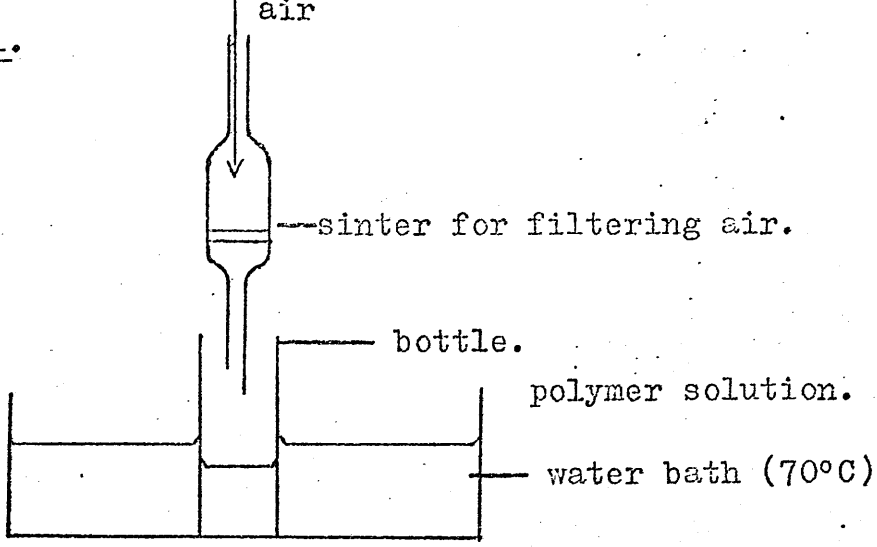


Fig.ix.

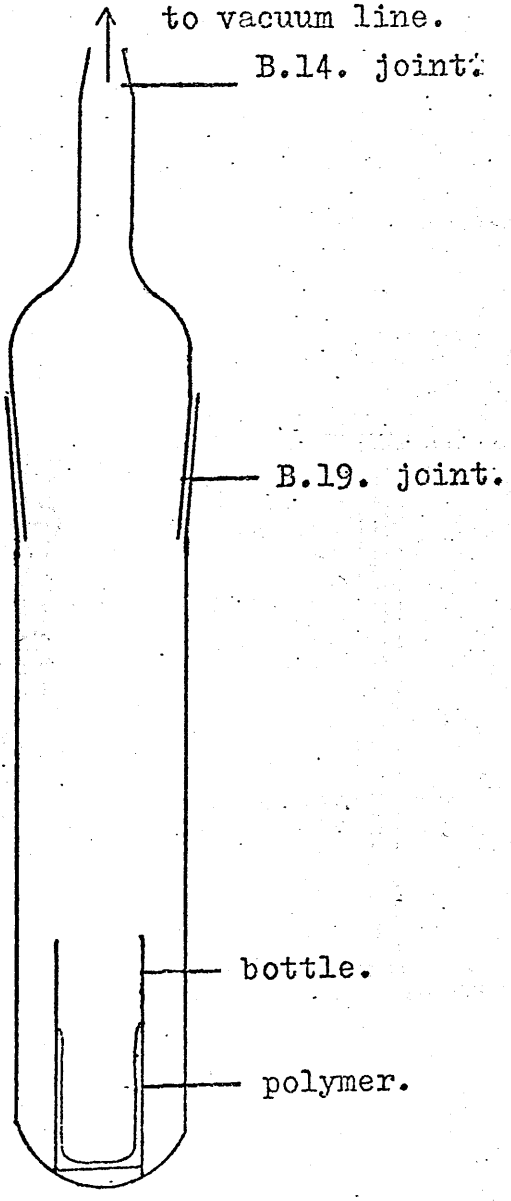


Fig.x.

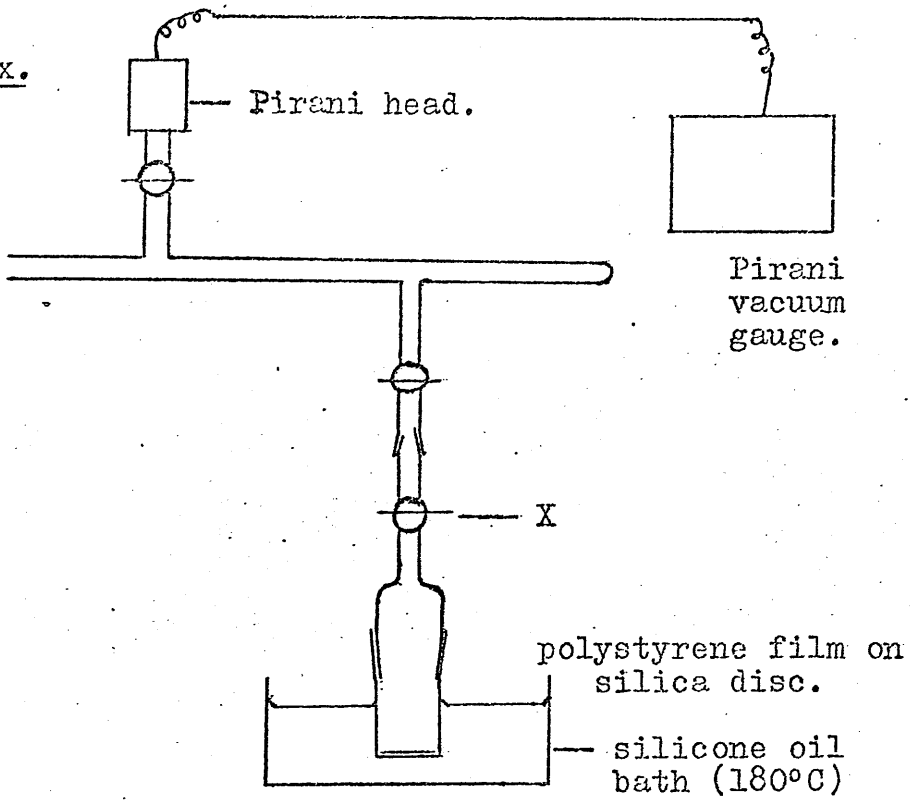

Pirani head.
Pirani vacuum gauge.
X
polystyrene film on silica disc.
silicone oil bath (180°C)

Fig.xi.

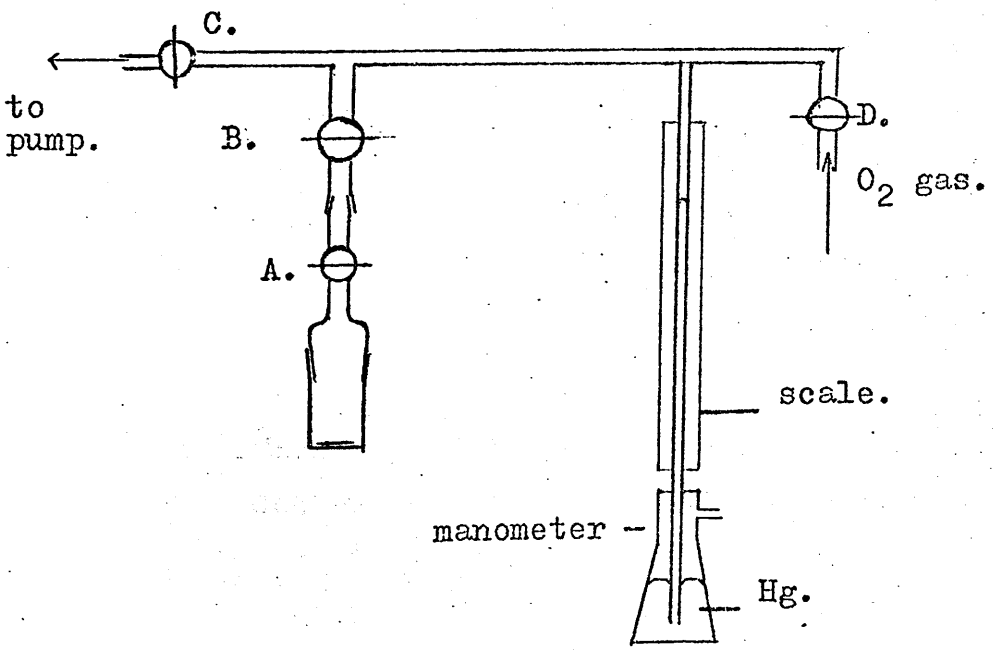

C.
to pump.
B.
A.
D.
O_2 gas.
scale.
manometer
Hg.

Fig. xii.

Typical Osmometer Data Plot.

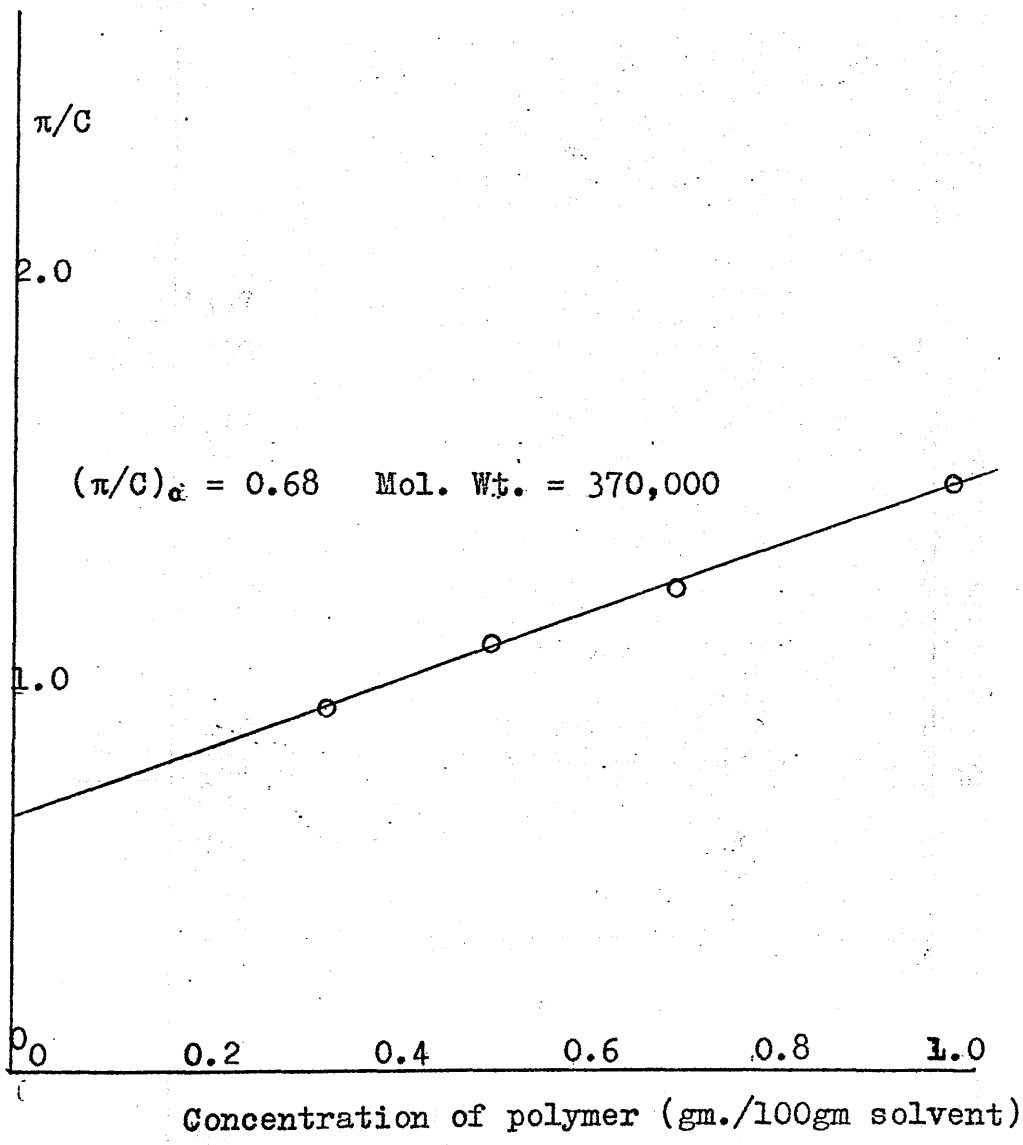


Fig. xiii.

Output of Hanovia Chromatolite Lamp.

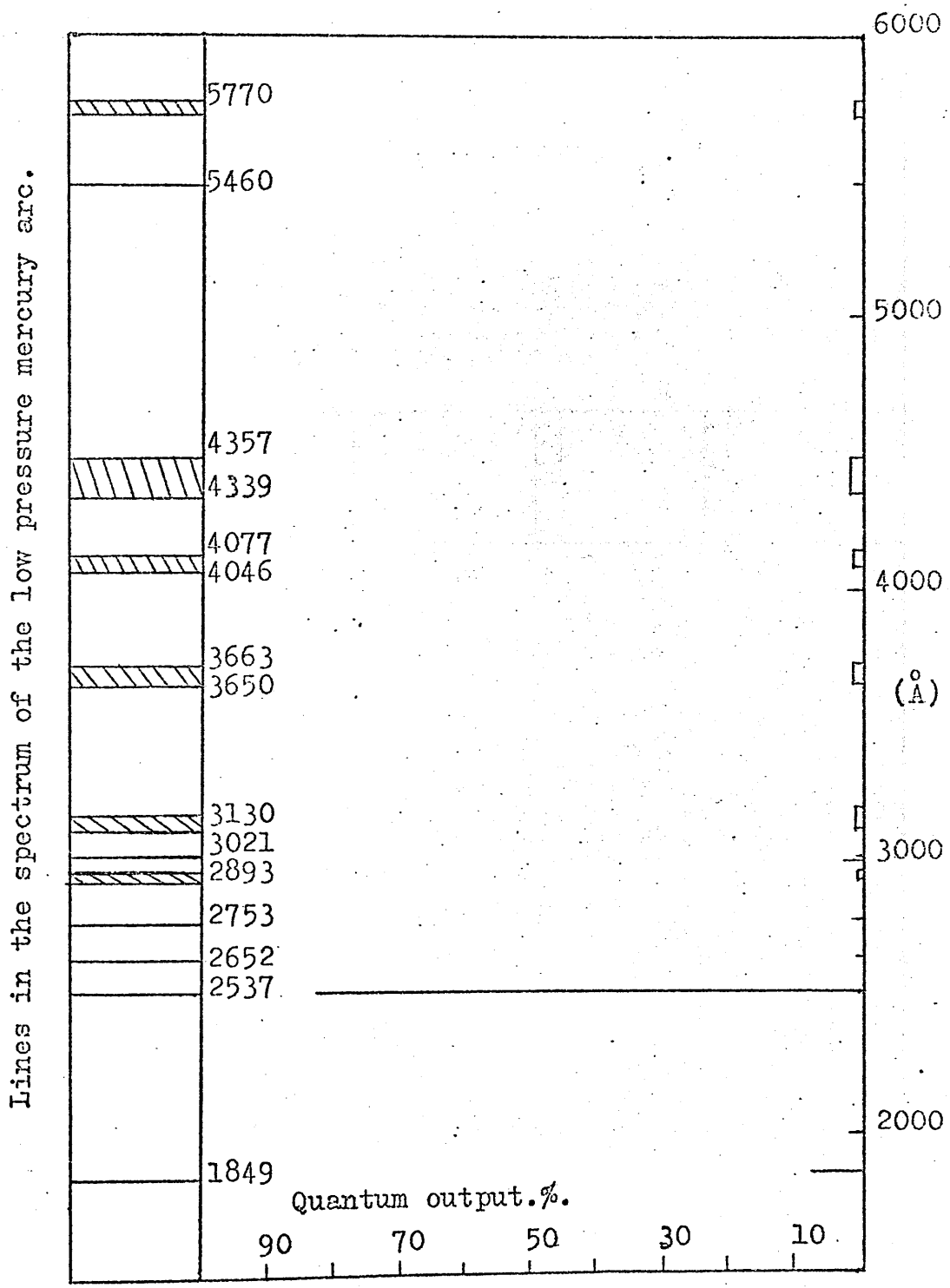


Fig.xiv.

Outputt of the Hanovia Fluorescence Lamp Model 11.

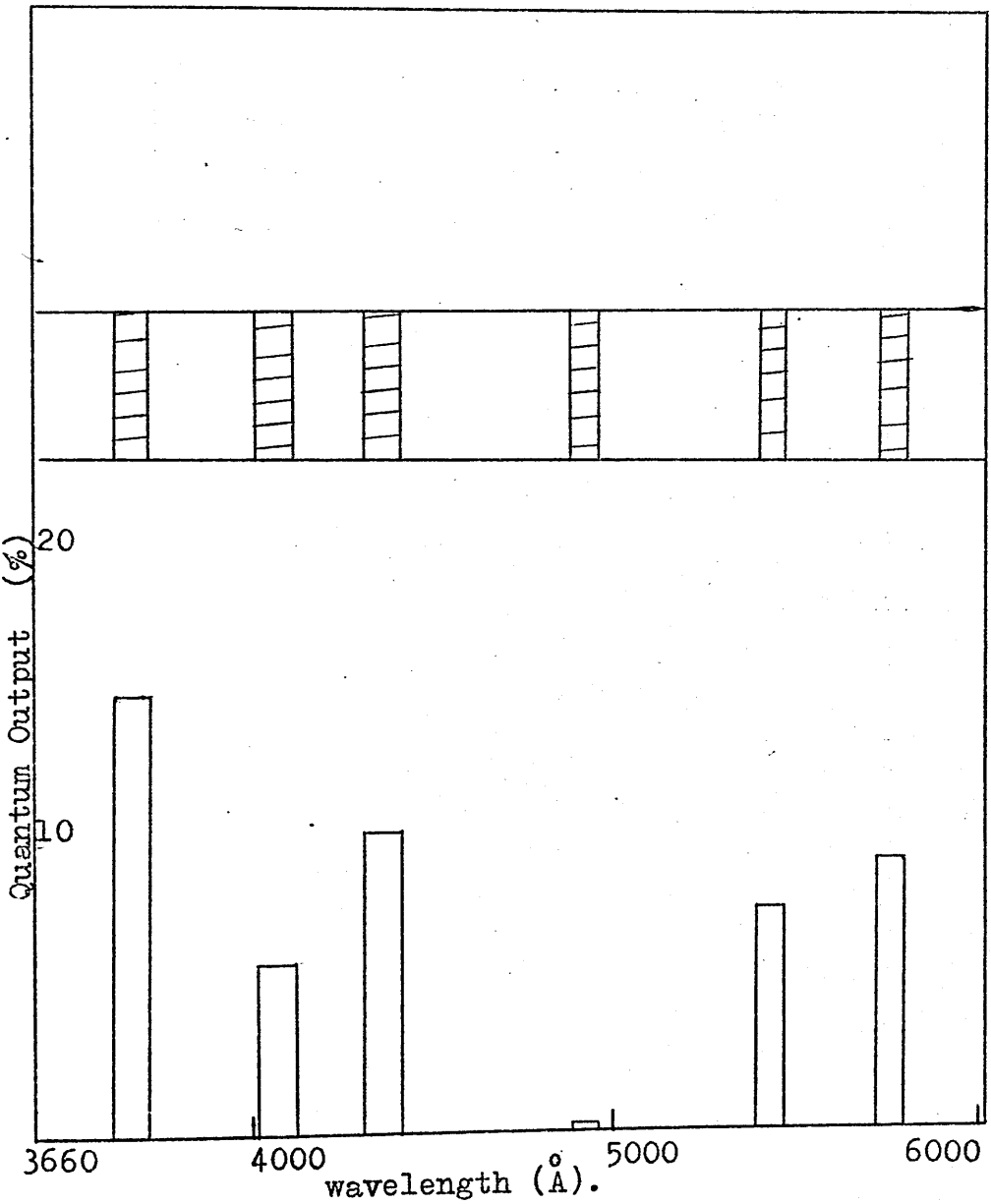


Fig. xv.

Ultra-violet absorption of Water.(1cm.)

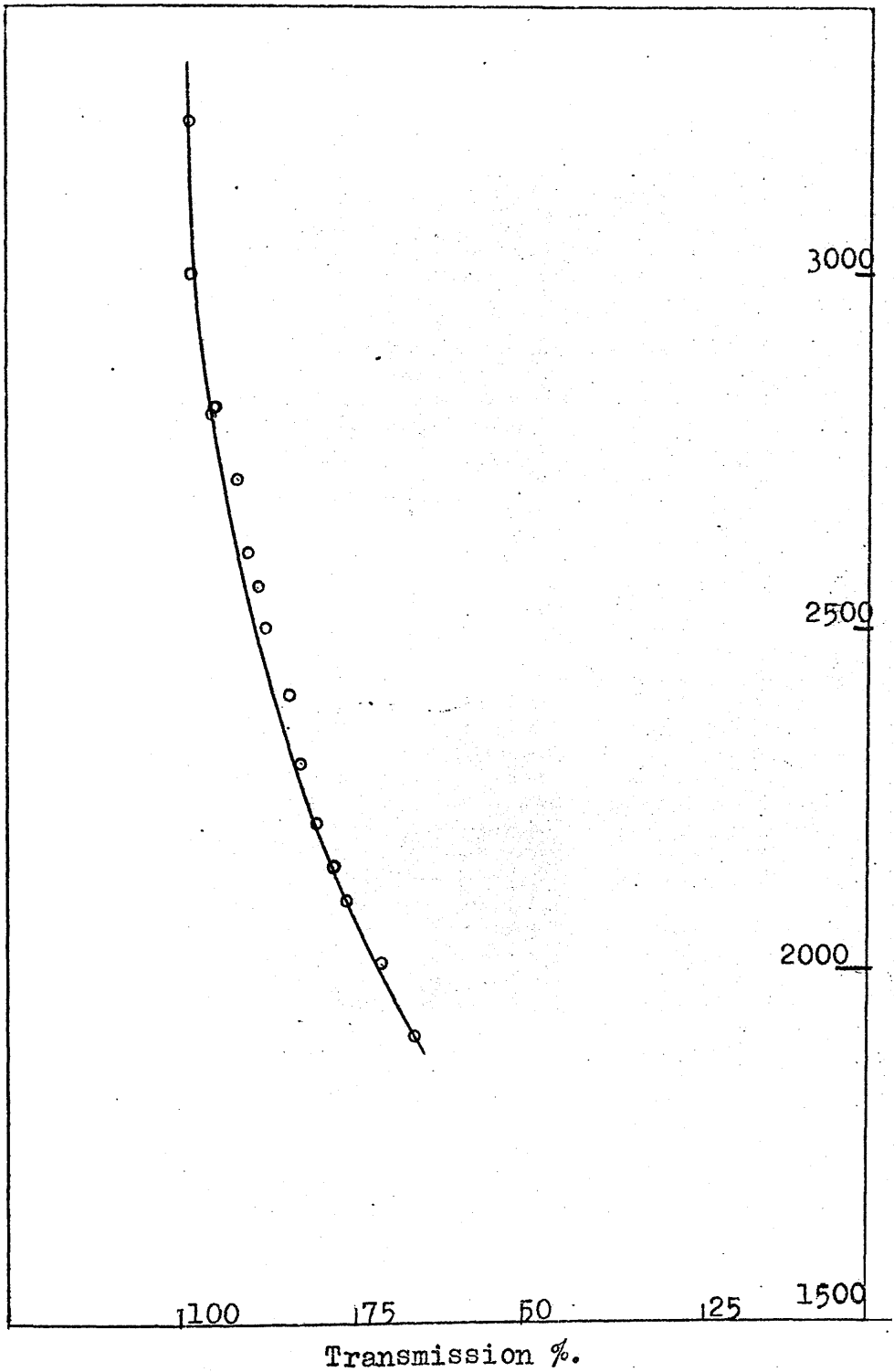
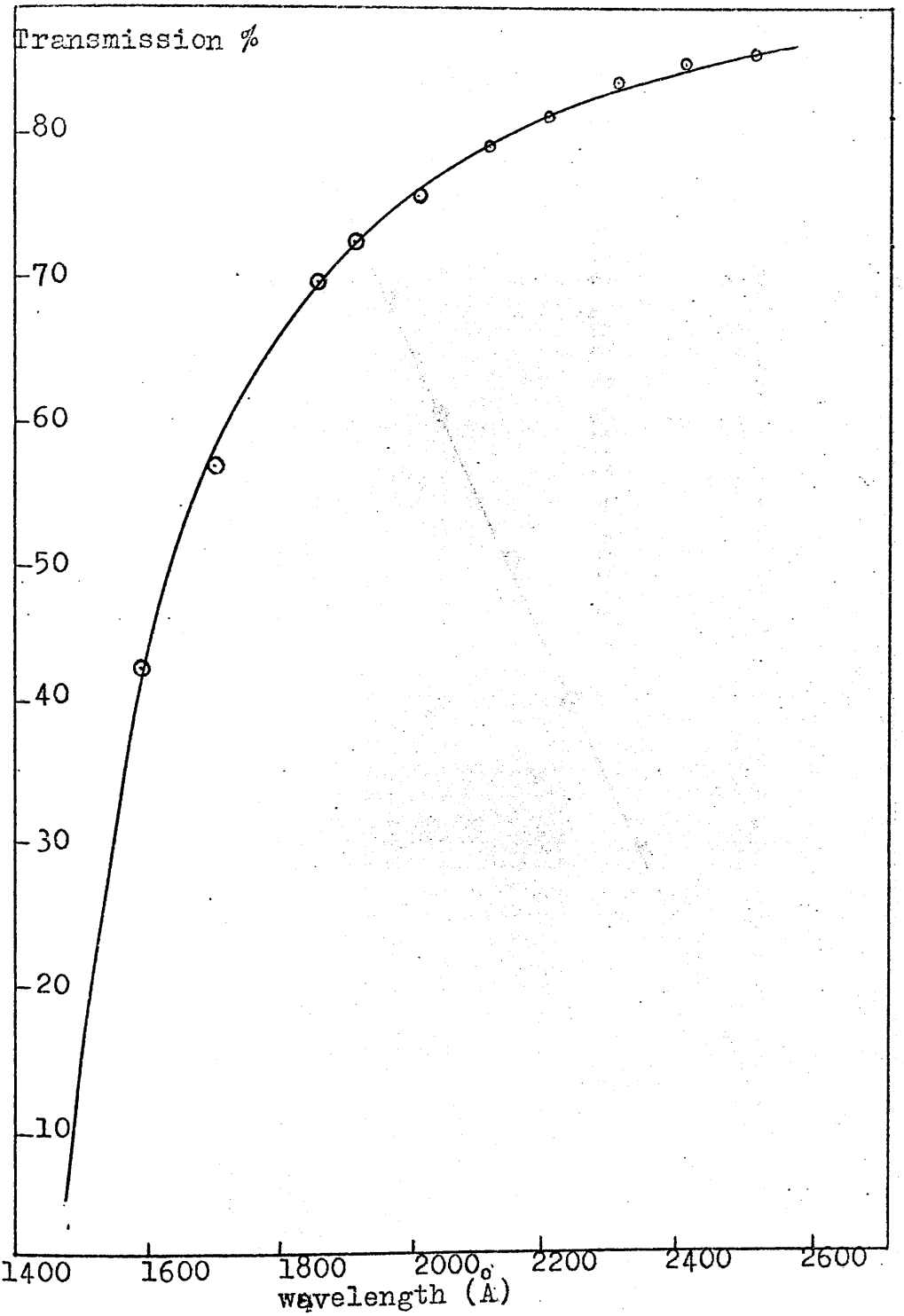


Fig. xvi. Absorption Spectrum of Fused Silica.



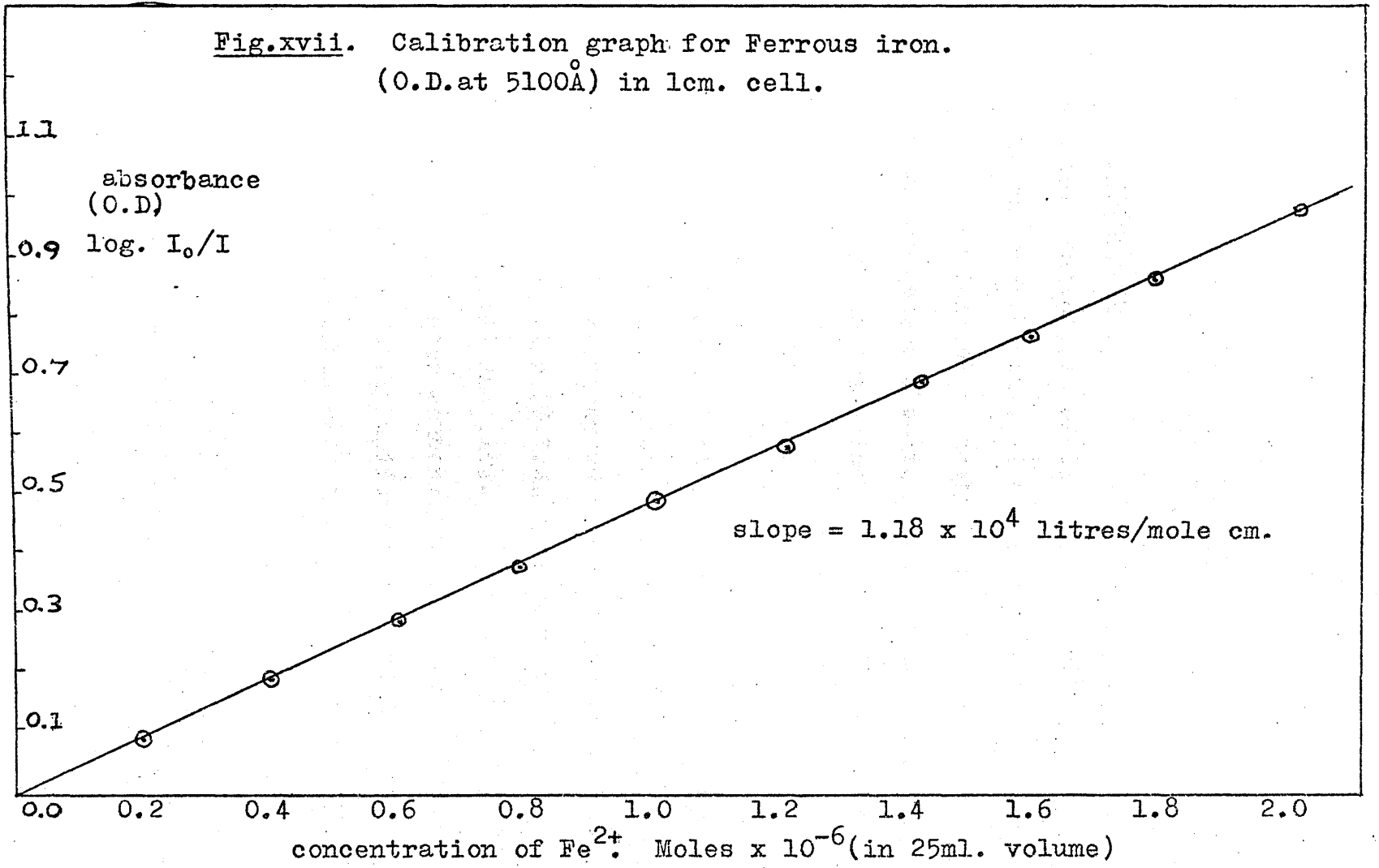


Fig.xvii. Calibration graph for Ferrous iron.
(O.D.at 5100Å) in 1cm. cell.
absorbance
(O.D)
log. I_o/I
1.1
0.9
0.7
0.5
0.3
0.1
slope = 1.18 x 10^4 litres/mole cm.
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
concentration of Fe^{2+}. Moles x 10^{-6}(in 25ml. volume)

CHAPTER 3.

PRELIMINARY OBSERVATIONS.

3.1. a. Introduction.

Before photolysis of the various polymers and copolymers was carried out, it was considered necessary to measure their molecular weights and molar compositions. It was necessary also to perform some control experiments to characterise the irradiation apparatus used.

b. Polymer samples.

The initiator concentrations used in the polymerisations, the molecular weights of the prepared samples and their molar compositions as predicted by the copolymer composition equation (2.1.c.) are presented in tables 3(i),(ii),(iii) and (iv). It can be seen that by varying the initiator concentration in the polymerisation mixtures, a fairly uniform degree of polymerisation was obtained within each copolymer composition range.

3.2. Copolymer composition data.

a. Copolymers of methyl methacrylate and methyl acrylate.

The molar compositions of these samples were

determined by nuclear magnetic resonance spectroscopy as described in chapter 2.10.c. The results of these measurements compared with the theoretical compositions according to the copolymer composition equation are shown in table 3.v.

b. Copolymers of methyl methacrylate and maleic anhydride.

1. Composition data.

As with copolymers of methyl methacrylate and methyl acrylate, this system does not incorporate a monomer containing a unique atom nor do the empirical formulae of the monomers differ to an extent which can be used as a basis for accurate determinations by elemental microanalysis. Blackley and Melville[64] noted that 1% error in elemental analysis of this system would lead to an error of 10% in the copolymer composition. Because of this, determinations by microanalysis were disregarded. For similar reasons of inaccuracy, determinations by n.m.r. spectroscopy were found to be unacceptable. N.m.r. spectra were obtained as in chapter 2.10.c., the anhydride protons expected to appear at about 7τ were not detected. The reason for this was that in the copolymer range under investigation, the copolymer composition ratio of methyl methacrylate to maleic anhydride was never

less than 10/1, thus, even for the copolymers richest in maleic anhydride, the ratio of "anhydride" protons to the "methacrylate" protons would be at least 40/1, much too large for the "anhydride" protons to be estimated with any degree of accuracy.

Infra-red spectra for each copolymer were recorded immediately after preparation and purification. 1mg. samples of polymer were ground up with 300mg. KBr and pressed to form a disc of which the spectrum was recorded.

Because of the abnormally high extinction coefficient of the anhydride group carbonyl stretching mode, the stretching vibration of the anhydride carbonyl at 1790cm.$^{-1}$ (5.6μ) was readily observed even in the 100/1 copolymer. For example, fig 3.1. shows the region of the carbonyl vibrational stretch for the 20/1 copolymer. However, it is necessary to match these spectra against standard spectra and to this end, mixtures of poly-(methyl methacrylate) and succinic anhydride were prepared, succinic anhydride being chosen as being similar to the anhydride group in the polymer. The basic assumption made here is that the extinction coefficient of the carbonyl stretching mode in succinic anhydride and

in the anhydride unit in the copolymer is the same so that direct comparison can be made between mixture and copolymer. The infra-red spectra of pure poly-(methyl methacrylate) and succinic anhydride were compared and it was found that the peaks at 1785cm.$^{-1}$(5.6μ) and 750cm.$^{-1}$ (13.5μ) were unique to the anhydride and polymer respectively. The spectra of these mixtures bore a close similarity to those of the copolymers. Even very small quantities of succinic anhydride(0.3×10^{-5}g.) gave rise to a readily identifiable peak at 1785cm.$^{-1}$ The absorbance or optical density of the anhydride carbonyl absorption peak was measured by drawing a base line for each peak as shown in fig.3.1.and reading off the transmittance at the peak height and base. These values were converted to absorbance and the base value subtracted from the peak height value. Since the value of absorbance thus obtained was not an absolute value it was necessary to refer to an internal reference in each spectrum. This was taken as the absorbance of the C-H bending mode at 750cm.$^{-1}$(13.5μ) which is unique to poly-(methyl methacrylate). Thus the ratio of anhydride absorbance to the methyl methacrylate absorbance is constant for any given mixture.

The results obtained by this method are shown in table 3.vi. where

$$X = \frac{\text{absorbance of succinic anhydride}}{\text{absorbance of methyl methyacrylate.}}$$

By calculating the ratio of the absorbance of the anhydride to the methyl methacrylate for the copolymers, the composition of the copolymers could be read off from the calibration graph in fig.3.ii. The results are shown in table 3.vii.

ii. Reactivity ratios r_1 and r_2.

Rearrangement of the copolymer composition equation(2.1.e.) gives the following relationship;

$$\frac{f_1(1 - 2F_1)}{(1 - f_1)F_1} = \frac{r_2 + f_1^2(F_1 - 1)}{(1 - f_1)^2 F_1}$$

where f_1 and F_1 are the mole fractions of methyl methacrylate in the monomer feed and the polymer respectively. This is the equation of a straight line with slope r_1 and intercept r_2. A least squares treatment of a series of points calculated from the copolymer composition yields the Fineman-Ross[72] plot shown in fig.3.iii.b. The values of r_1 and r_2 obtained from this plot are

$r_1 = 3.36$

$r_2 = 0.04$., these values agreeing well

with those quoted by Blackley and Melville[64],

$r_1 = 3.5$

$r_2 = 0.03$, the plot from which is also shown in fig.3.iii.a.

c. Copolymers of methyl methacrylate and styrene, and methyl methacrylate and methacrylonitrile.

Since in both of these copolymer systems one of the monomers contains an exclusive atom the method of elemental analysis was used to determine the copolymer compositions. With copolymers of methacrylonitrile the composition could be calculated on the basis of either the percentage nitrogen or percentage oxygen present in the samples. However, the percentage nitrogen is a direct measurement and it was used since the oxygen determination is obtained by difference and any error in the determinations of the other elements would accumulate in the value obtained for oxygen. With the styrene copolymers the calculation was based on oxygen content. It can be seen from tables 3.viii. and 3.ix. that in both cases the compositions obtained agree well with those which were theoretically predicted.

3.3 Calibration of the Photolysis Apparatus.

Before making a systematic investigation of the photolysis of copolymers of methyl methacrylate and methyl acrylate, it was considered necessary to study the characteristics of the degradation apparatus, in particular the photolysis cells and lamp, since in this work, four different photolysis cells were used in combination with four different irradiation positions on the lamp. To do this, a number of irradiations of a solution of poly-(methyl acrylate) in methyl acetate (20mg./ml.) were carried out, varying separately the cell employed and its irradiation position with respect to the lamp. The molecular weights determined after irradiation are summarised in table 3x. The polymer solution was irradiated in photolysis cell number 1 for 1 hour on four separate occasions and the molecular weights of the irradiated polymer obtained are shown in section A of table 3.x. There is obviously good agreement between the calculated number of chain scissions occurring, indicating good reproducibility of the irradiation and molecular weight determination processes.

Section B summarises the result obtained when, to test the interchangeability of the photolysis cells,

the solution of poly-(methyl acrylate) was irradiated within each of the four different cells using only one (I) position of the irradiation source. Column 5 of table 3.x. shows that the number of scissions is approximately equal for each irradiation, illustrating that for the purposes of this work the transmission characteristics of all four photolysis cells are the same and that they are completely interchangeable.

Section C deals with the results obtained after irradiations performed with the same photolysis cell clamped in turn in each of the four irradiation positions of the apparatus, as shown in fig.2.v. Once again column 5 shows good agreement indicating that for the purposes of this investigation, the intensity of the radiation incident on the cells is equal, within experimental error, at the four positions on the lamp.

3.4. Photolysis of Poly-(methyl acrylate).

Before studying the detailed characteristics of the photodegradation of the copolymer systems in solutions, some preliminary work was carried out on solution photolysis of poly-(methyl acrylate) to clarify some questions concerning the fundamental aspects of this type of work.

a. Extent of chain scission with increasing time of irradiation.

Solutions of poly-(methyl acrylate) in methyl acetate were irradiated with half hour increments for periods up to four hours. The molecular weight and chain scission data obtained are shown in table xi. and plotted in fig.3.iv. Fig.3.iv. shows chain scission increasing linearly with time of irradiation and thus the quantity of radiation absorbed. This indicates that the chain scission reaction occurring is a randomly initiated process. The rate of chain scission per monomer unit per hour is obtained from the slope of the graph.

b. Rate of chain scission in different solvents.

Before any comparison of the observed rates of chain scission of poly-(methyl acrylate) in different solvents could be carried out, any attenuation of the incident radiation by the solvents used must be determined. Ultra-violet spectra of the solvents were obtained and are shown in fig.3.v. Methylene chloride, chloroform and methyl acetate all show intense absorption in the region 2400-2000Å with at least 70% transmission in the 2537Å region. However, in the case of benzene the strongly absorbing aromatic ring completely absorbs

radiation in the 2537Å region.

Solutions of poly-(methyl acrylate) (20mg./ml.) in methylene chloride, chloroform and benzene were prepared, irradiated and the rates of chain scission investigated. The results obtained are shown in tables3.xi, xii,xiii and xiv. and the rates of chain scission obtained from the slopes are shown in fig 3.vi. The data on fig. 3.vi. indicate that within the error inherent in molecular weight determinations by osmometry, the rates of chain scission of poly-(methyl acrylate) in solutions of methylene chloride, chloroform and methyl acetate are very similar, and that slight differences in solvent attenuation of the incident radiation can be ignored. However, the rate of chain scission in solutions of benzene is very small compared with the other solvents, this arising from the very strong optical filter effect since benzene completely absorbs the degradative radiation at a wavelength of 2537Å. Since the rates of degradation in solvents chloroform, methylene chloride and methyl acetate are similar, it appears that any direct solvent participation in the chain scission reaction by the production of free radicals (eg. $CH_3^{\bullet}$, $Cl^{\bullet}$ or $CHCl_2^{\bullet}$) which could attack the polymer chain, must be very small

compared with reactions following absorption of energy by the polymer itself. Although the possibility of production of free radicals from the solvent cannot be ruled out, it appears that the majority if radicals formed are quenched through reaction with other solvent molecules present, and that the primary role of the solvents in this case is that of an optical filter.

c. Chain scission dependence on polymer concentration.

If the solvents were functioning chemically in some way other than as optical filters it is likely that changing the relative concentrations of the polymer and solvent would have some effect on the rates of the chain scission reaction. Solutions of poly-(methyl acrylate) in chloroform and methyl acetate covering a ten fold concentration range (1%-10%W/V) were irradiated and the data obtained are shown in tables xv. -- xviii. and are plotted in figs. vii -- xvii. The rates of chain scission obtained from the slopes of figs.vii -- xvii. plotted against solution concentration are shown in fig.xviii. In the case of both chloroform and methyl acetate solution irradiations, the best fitting curve is an almost horizontal straight line indicating that the scission reaction is not dependent upon polymer concentration.

This lends weight to the earlier suggestion that the solvents are not participating in any significant way other than as optical filters.

d. Photolysis with radical initiator.

To test the above conclusion further, a solution of poly-(methyl acrylate) containing a known radical initiator (2,2' azo-bis-isobutyronitrile 1%W/V) was irradiated and the data obtained are shown in table ixx. and fig.ixx. The rate obtained from the slope of the graph is not sufficiently different from that obtained previously in the absence of radical initiator.

e. Crosslinking of poly-(methyl acrylate).

As discussed in chapter 1, polymers containing tertiary carbon atoms in their backbone (eg. poly-[methyl acrylate]) are well known for their ability to crosslink in the solid state under the influence of U.V. radiation. However in the solution studies described here, no insolubility of the irradiated polymer was ever observed.

f. Variation of radiation intensity with distance from the source.

To test this variable, solutions of poly-(methyl acrylate) 20mg./ml. in methyl acetate were irradiated at a distance of 20cm. from the radiation source and the

data obtained are shown in table xx. and plotted in fig.xx.(line a.). Line(b) is the average slope obtained for irradiation at 10 cm.,obtained from fig.xviii. The slope of line(a) yields the rate of chain scission as 0.40 scissions per monomer unit per hour as compared with 1.4 scissions per monomer unit per hour for irradiations at 10cm. distance. If the intensity of radiation varied with the inverse square of the distance from the lamp, as for a point source, the rate expected would be;

$$1.4 \times (10/20)^2 \text{ scissions/monomer unit/hour.}$$

$$= 0.35 \text{ scissions/monomer unit/hour.}$$

The intensity of radiation would seem to be slightly greater than that predicted by the inverse square law, probably attributable to the fact that the light source is a cylindrical,rather than a point source.

g. Irradiation by 3660Å radiation.

Solutions of poly-(methyl acrylate) in methyl acetate were irradiated using 3660Å radiation as described in chapter 2, the data in table xxi. being obtained. Although chain scission does occur, it is negligible compared with that resulting from 2537Å radiation.

h. Spectroscopic Determinations.

Infra-red and ultra-violet spectra of unirradiated and irradiated samples of poly-(methyl acrylate) in chloroform were recorded. There was no change in the infra-red spectra on irradiation and only a slight general increase in absorption in the 4000Å region of the ultra-violet spectra spectrum.

Table 3.i.

Methyl methacrylate(MMA)/methyl acrylate(MA) copolymers.

Projected composition.	Initiator concentration.	Molecular weight.
100% MA.*	0.25% W/V.	360,000
89% MA.	0.1 % W/V	350,000
70% MA.	0.1 % W/V	240,000
66% MA.	0.1 % W/V	330,000
60% MA.	0.1 % W/V	500,000
50% MA.	0.15% W/V	250,000
30% MA.	0.1 % W/V	300,000
15% MA.	0.1 % W/V	550,000
100% MMA.	0.1 % W/V	370,000

* denotes solution polymerisation

Table 3.ii.

Methyl methacrylate/Styrene copolymers.

Projected composition.	Initiator concentration.	Molecular weight.
100% styrene	0.03% W/V	250,000
90% styrene	0.03% W/V	280,000
80% styrene	0.03% W/V	250,000
60% styrene	0.04% W/V	260,000
40% styrene	0.04% W/V	270,000
20% styrene	0.05% W/V	250,000
10% styrene	0.05% W/V	300,000
100% MMA.	0.10% W/V	370,000.

Table 3.iii.

Methyl methacrylate/methacrylonitrile(MAN) copolymers.

Projected composition.	Initiator concentration.	Molecular weight.
100% MAN.	0.025% W/V	122,000
90% MAN.	0.025% W/V	95,000
80% MAN.	0.05% W/V	95,000
60% MAN.	0.10% W/V	188,000
50% MAN.	0.10% W/V	109,000
30% MAN.	0.15% W/V	97,000
20% MAN.	0.20% W/V	101,000
10% MAN.	0.20% W/V	150,000

Table 3.iv.

Methyl methacrylate/maleic anhydride(Mal.A) copolymers.

Projected composition. MMA/Mal.A.	Initiator concentration.	Molecular weight.
100 : 1	0.1% W/V	345,000
50 : 1	0.1% W/V	454,000
20 : 1	0.1% W/V	50,000
10 : 1	0.1% W/V	122,000
PMMA.	0.1% W/V	513,000

Table 3.v.

Composition of copolymers of methyl methacrylate and methyl acrylate.

Theoretical composition % MA.	Composition from n.m.r. data.
89%	90%
70%	70%
66%	70%
60%	50%
50%	50%
30%	30%
15%	15%

Table 3.vi.

Mixture	% poly-(methyl methacrylate)	X.	Scan speed.
100/1	99.01	0.794	fast
		0.855	slow
		1.000	fast
		1.000	medium
50/1	97.88	1.68	fast
		1.73	medium
		1.65	fast
20/1	95.65	2.015	fast
		2.33	fast
		2.41	medium
15/1	93.99	2.49	fast
		2.44	fast
		2.63	medium
		2.45	fast
		2.49	medium
10/1	91.45	3.77	fast
		3.98	medium
		3.78	fast
		3.88	medium
12/1	92.44	3.34	fast
		3.65	medium
18/1	94.48	2.27	fast
		2.11	fast
		2.43	medium

Table 3.vii.

Copolymer	X	%methyl methacrylate
100 : 1	1.186	98.4
50 : 1	1.76	97.0
20 : 1	3.08	93.8
10 : 1	3.30	93.2

Table 3.viii.

Composition of methyl methacrylate/methacrylonitrile copolymers.

Theoretical composition mole% MAN.	Theoretical %nitrogen by weight.	Experimental %nitrogen by weight	Actual composition mole% MAN.
90	17.9	17.4	88
80	15.2	15.1	79
60	10.45	10.9	62
50	8.39	9.21	54
30	4.62	5.55	35
20	3.00	3.48	23
10	1.45	1.75	12

Table 3.ix.

Composition of methyl methacrylate/styrene copolymers.

Theoretical composition mole% styrene.	Theoretical % oxygen by weight.	Experimental % oxygen by weight.	Actual composition mole%styrene.
90	3.09	3.03	90
80	6.20	5.84	80
60	12.50	11.87	60
40	18.90	18.28	40
20	25.41	25.21	20
10	28.60	28.60	10
PMMA	32.00	31.62	-

Table 3.x.

Calibration of Photolysis Cells and Irradiation Source.

	Cell	Position on lamp.	Time of irradiation	Molec. weight.	Scissions per monomer unit.
A.	I	I	1.0 hours	234,000	1.29×10^{-4}
	I	I	1.0 hours	228,000	1.36×10^{-4}
	I	I	1.0 hours	236,000	1.26×10^{-4}
	I	I	1.0 hours	235,000	1.31×10^{-4}
B.	I	I	1.0 hours	234,000	1.29×10^{-4}
	II	I	1.0 hours	236,000	1.26×10^{-4}
	III	I	1.0 hours	233,000	1.30×10^{-4}
	IV	I	1.0 hours	238,000	1.22×10^{-4}
C.	I	I	1.0 hours	234,000	1.29×10^{-4}
	I	II	1.0 hours	232,000	1.30×10^{-4}
	I	III	1.0 hours	230,000	1.34×10^{-4}
	I	IV	1.0 hours	237,000	1.24×10^{-4}

Tables 3.xi. and 3.xii.

Irradiation of poly-(methyl acrylate) in Chloroform.

Time (hrs.) Irradiation.	Molecular Weight.	Scissions per Monomer unit.
0.5	264,000	0.86×10^{-4}
1.0	221,000	1.69×10^{-4}
1.5	195,000	2.02×10^{-4}
2.0	167,000	2.76×10^{-4}
2.5	144,000	3.58×10^{-4}
3.0	137,000	3.95×10^{-4}
3.5	118,000	4.87×10^{-4}
4.0	110,000	5.30×10^{-4}

Irradiation of poly-(methyl acrylate) in Methyl Acetate.

Time (hrs.) Irradiation.	Molecular Weight	Scissions per Monomer unit.
0.5	294,000	0.54×10^{-4}
1.0	220,000	1.50×10^{-4}
1.5	190,000	2.12×10^{-4}
2.0	171,000	2.70×10^{-4}
2.5	160,000	2.98×10^{-4}
3.0	144,000	3.58×10^{-4}
3.5	140,000	3.79×10^{-4}
4.0	120,000	4.75×10^{-4}

Table 3.xiii.

Irradiation of poly-(methyl acrylate) in Methylene chloride.

Time (hrs.) Irradiation.	Molecular Weight.	Scissions per Monomer unit.
1.0	248,000	1.09×10^{-4}
2.0	183,000	2.3×10^{-4}
3.0	135,000	4.0×10^{-4}
4.0	125,000	4.5×10^{-4}

Table 3.xiv.

Irradiation of poly-(methyl acrylate) in Benzene.

Time (hrs.) Irradiation.	Molecular Weight.	Scissions per Monomer unit.
1.0	360,000	0
2.0	350,000	0.07×10^{-4}
3.0	339,000	0.14×10^{-4}
4.0	333,000	0.19×10^{-4}

Table 3.xv.

Irradiation of poly-(methyl acrylate) in solutions of varying concentration in Methyl Acetate.

Concentration of solution.	Time (hrs.) Irradiation.	Molecular Weight.	Scissions per Monomer unit.
1% W/V.	0.5	250,000	1.07×10^{-4}
	1.0	240,000	1.2×10^{-4}
	1.5	175,000	2.5×10^{-4}
	2.0	155,000	3.15×10^{-4}
	2.5	155,000	3.15×10^{-4}
	3.0	130,000	4.20×10^{-4}
	4.0	116,000	5.00×10^{-4}
1.5% W/V.	0.5	230,000	1.3×10^{-4}
	1.0	203,000	1.79×10^{-4}
	1.5	184,000	2.28×10^{-4}
	2.0	154,000	3.21×10^{-4}
	2.5	138,000	3.82×10^{-4}
	3.0	122,000	4.65×10^{-4}
	3.5	110,000	5.40×10^{-4}
	4.0	110,000	5.40×10^{-4}
2.0% W/V.	1.0	210,000	1.71×10^{-4}
	1.5	177,000	2.38×10^{-4}
	2.0	174,000	2.56×10^{-4}
	2.5	169,000	2.70×10^{-4}
	3.0	144,000	3.58×10^{-4}
	3.5	123,000	4.50×10^{-4}
	4.0	112,000	5.30×10^{-4}

Table 3.xv. (continued)

Concentration of solution.	Time (hrs.) Irradiation.	Molecular Weight.	Scissions per Monomer unit.
2.5%W/V.	see table 3.xii.		
5.0%W/V.	1.0	246,000	1.14×10^{-4}
	2.0	210,000	1.72×10^{-4}
	2.66	154,000	3.20×10^{-4}
	3.25	145,000	3.52×10^{-4}
	4.0	115,000	5.00×10^{-4}
8%W/V.	1.0	220,000	1.51×10^{-4}
	2.0	165,000	2.81×10^{-4}
	3.0	124,000	4.50×10^{-4}
	4.0	110,000	5.37×10^{-4}
10%W/V.	1.0	246,000	1.19×10^{-4}
	1.5	206,000	1.78×10^{-4}
	2.5	170,000	2.62×10^{-4}
	3.0	142,000	3.67×10^{-4}
	3.5	132,000	4.10×10^{-4}
	4.25	122,000	4.65×10^{-4}

Table 3.xvi.

Concentration of polymer in methyl acetate soln.	No. of chain scissions per monomer unit/hour.
1% W/V.	1.48×10^{-4}
1.5%W/V	1.50×10^{-4}
2.0%W/V	1.33×10^{-4}
2.5%W/V	1.40×10^{-4}
5.0%W/V	1.20×10^{-4}
8.0%W/V	1.46×10^{-4}
10.0%W/V	1.20×10^{-4}

Table 3.xvii.

Irradiation of poly-(methyl acrylate) in solutions of varying concentration in Chloroform.

Concentration of solution.	Time(hrs.) Irradiation.	Molecular Weight.	Scissions per Monomer unit.
1.0%W/V.	1.0	250,000	1.05×10^{-4}
	1.5	204,000	1.82×10^{-4}
	2.0	171,000	2.62×10^{-4}
	2.5	150,000	3.33×10^{-4}
	3.0	130,000	4.20×10^{-4}
	3.5	121,000	4.75×10^{-4}
	4.5	110,000	5.45×10^{-4}
1.5%W/V	0.5	298,000	0.5×10^{-4}
	1.0	209,000	1.71×10^{-4}
	1.5	183,000	2.30×10^{-4}
	2.5	158,000	3.04×10^{-4}
	3.0	138,000	3.83×10^{-4}
	3.5	121,000	4.70×10^{-4}
	4.5	111,000	5.35×10^{-4}
2.0%W/V	0.5	276,000	0.74×10^{-4}
	1.5	190,000	2.12×10^{-4}
	2.0	170,000	2.62×10^{-4}
	2.5	195,000	1.91×10^{-4}
	3.0	142,000	3.67×10^{-4}
	3.75	128,000	4.30×10^{-4}
	4.25	120,000	4.76×10^{-4}
2.5%W/V	see table 3.xii.		
9.0%W/V	1.0	206,000	1.77×10^{-4}
	2.0	152,000	3.26×10^{-4}
	3.0	132,000	4.10×10^{-4}
	4.0	104,000	5.80×10^{-4}

Table 3. xviii.

Concentration of polymer in Chloroform solution.	No. of chain scissions per monomer unit/hour.
1.0%W/V.	1.3×10^{-4}
1.5%W/V	1.3×10^{-4}
2.0%W/V	1.18×10^{-4}
2.5%W/V	1.2×10^{-4}
9.0%W/V	1.41×10^{-4}

Table 3. xix.

Photolysis of poly-(methyl acrylate) plus azo-bis-isobutyronitrile (10%W/V) in Methyl Acetate.

Time (hrs.) of Irradiation.	Molecular Weight.	Scissions per Monomer unit.
0.5	266,000	0.84×10^{-4}
1.0	245,000	1.12×10^{-4}
1.5	215,000	1.62×10^{-4}
2.0	195,000	2.02×10^{-4}
2.5	162,000	2.91×10^{-4}
4.0	135,000	3.97×10^{-4}

Table 3.xx.

Irradiation of poly-(methyl acrylate) solutions at a distance of 20cm. from the radiation source.

Time (hrs.) of Irradiation.	Molecular Weight.	Scissions per Monomer unit.
1.0	300,000	0.47×10^{-4}
3.0	245,000	1.12×10^{-4}
4.0	230,000	1.36×10^{-4}
6.5	162,000	2.91×10^{-4}

Table 3.xxi.

Irradiation of poly-(methyl acrylate) solutions by 3660Å wavelength radiation.

Time (hrs.) of Irradiation.	Molecular Weight.	Scissions per Monomer unit.
12	300,000	0.48×10^{-4}
24	250,000	1.03×10^{-4}

Rate of chain scission = 0.04×10^{-4} /monomer unit/hr.

Fig. 3.i. Carbonyl Stretch Region for 20/1 Copolymer of Methyl Methacrylate and Maleic Anhydride.

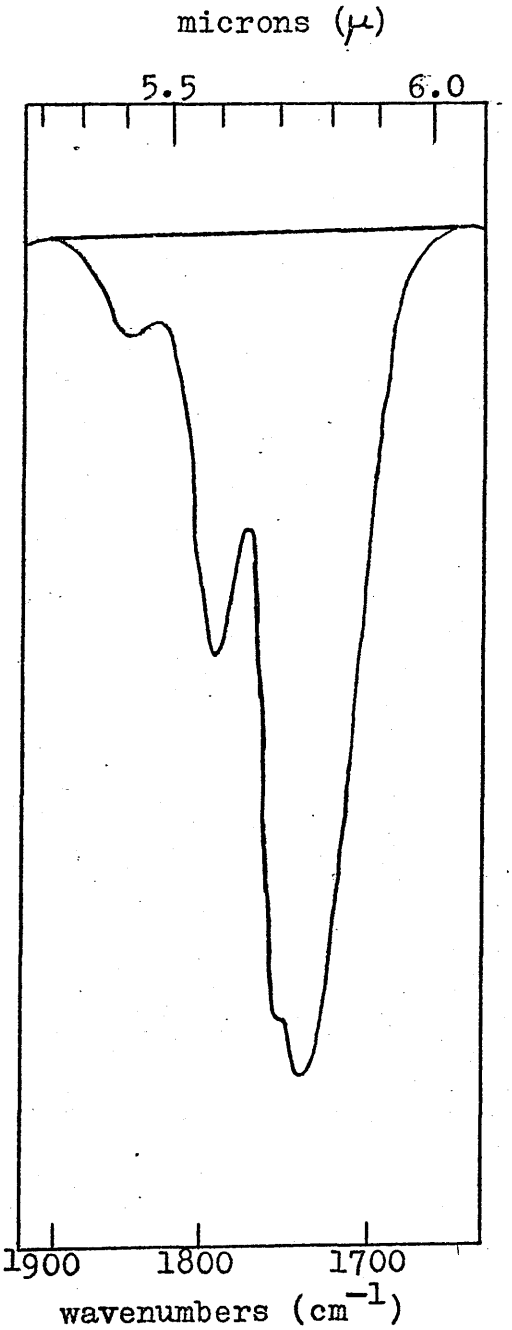


Fig.3.ii.

Absorbance of Succinic Anhydride/absorbance of poly-(Methyl Methacrylate),(X), vs. % Methyl Methacrylate.

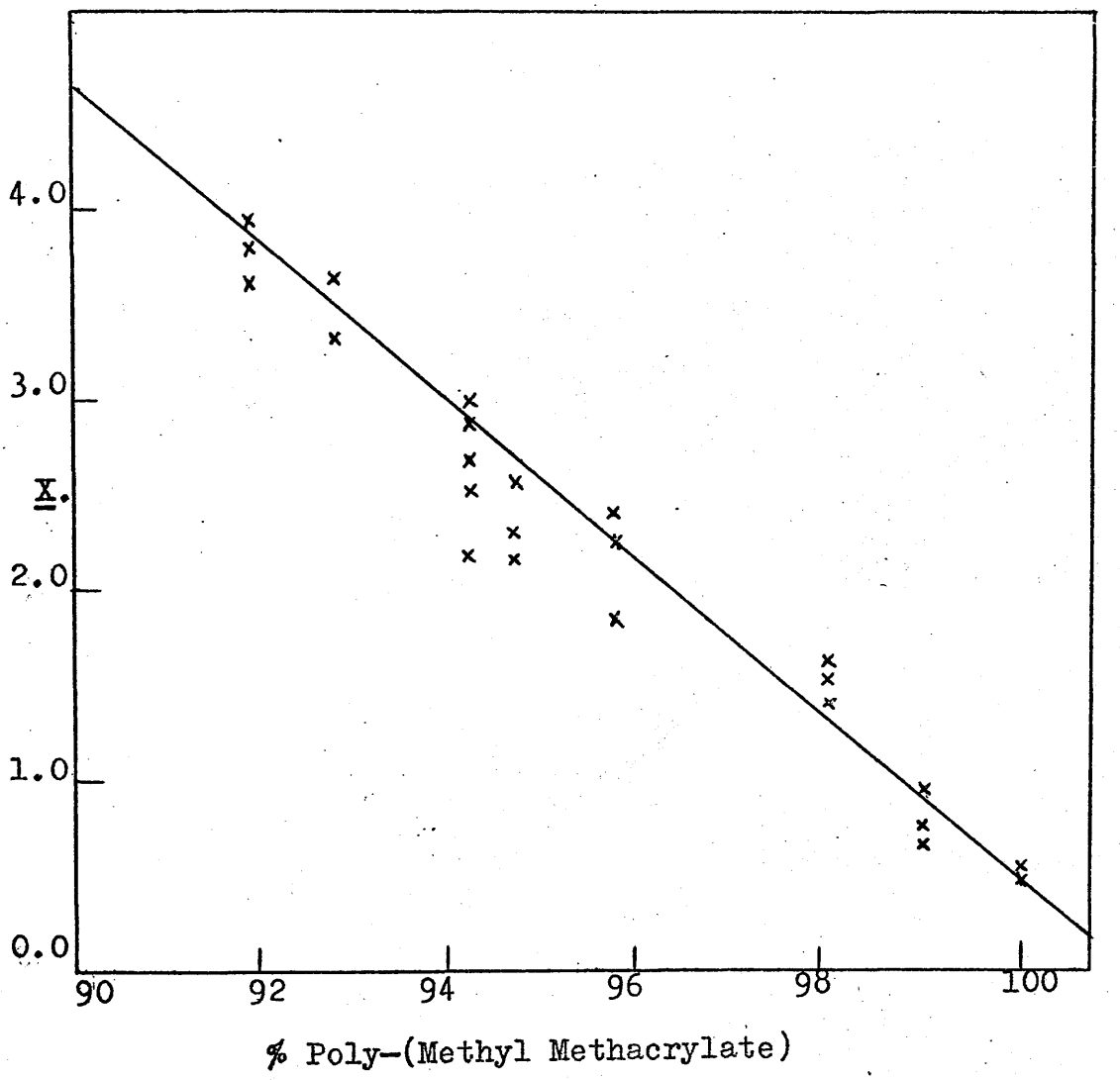


Fig. 3.iii.

Fineman-Ross plot for Copolymers of Methyl Methyacrylate and Maleic Anhydride.

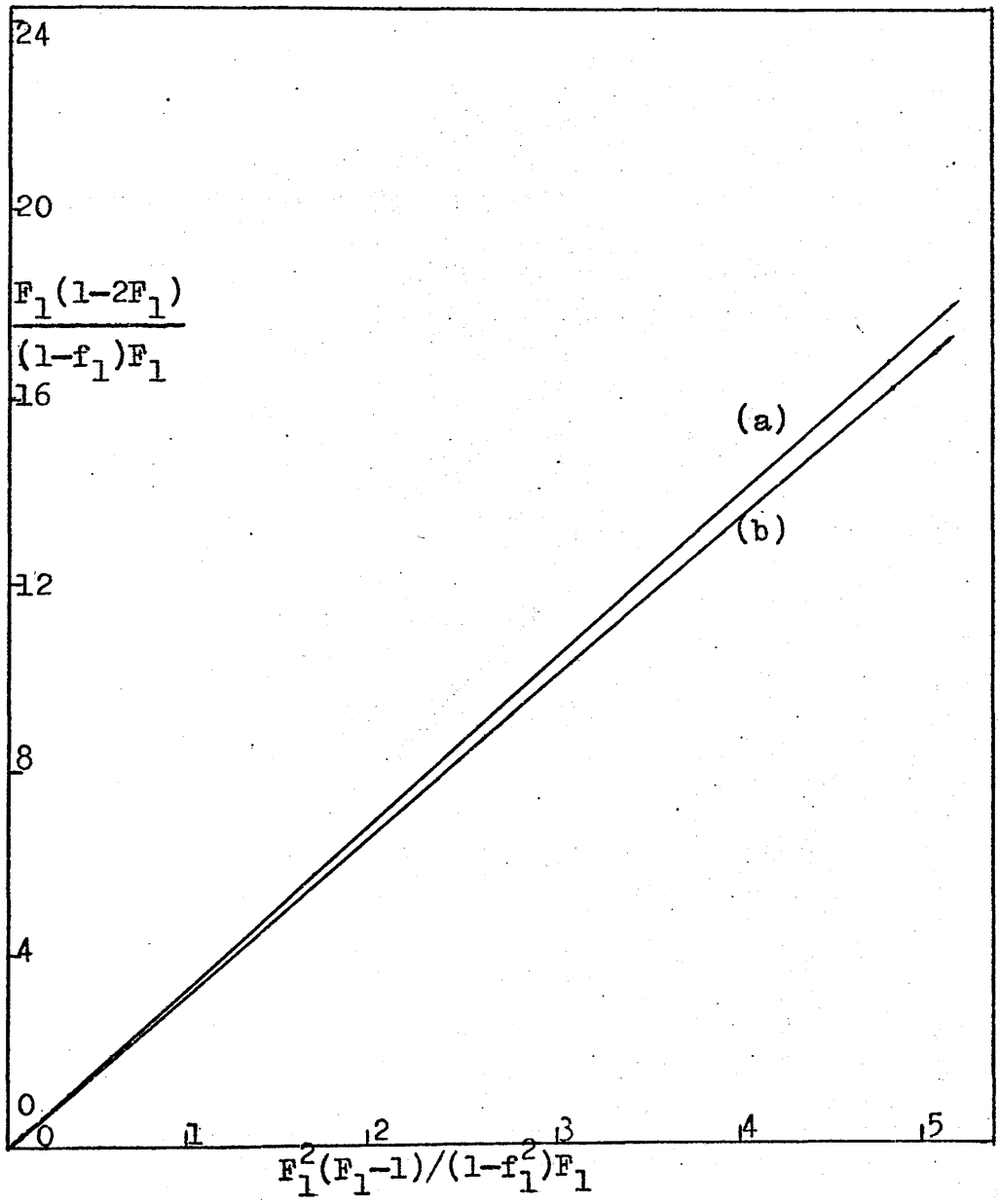
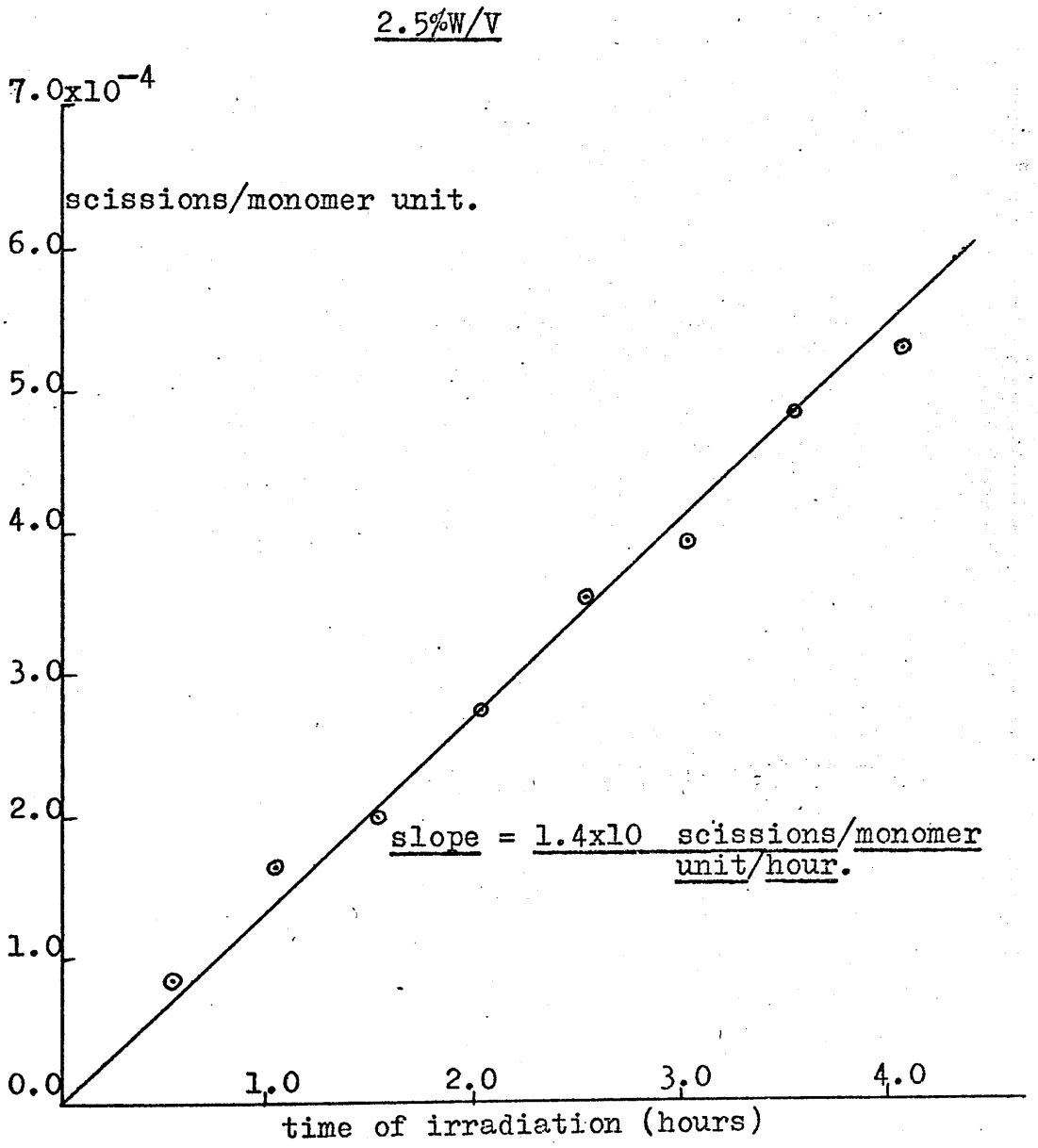


Fig.3.iv. Irradiation of poly-(methyl acrylate).

Scissions/monomer unit vs. time of irradiation.



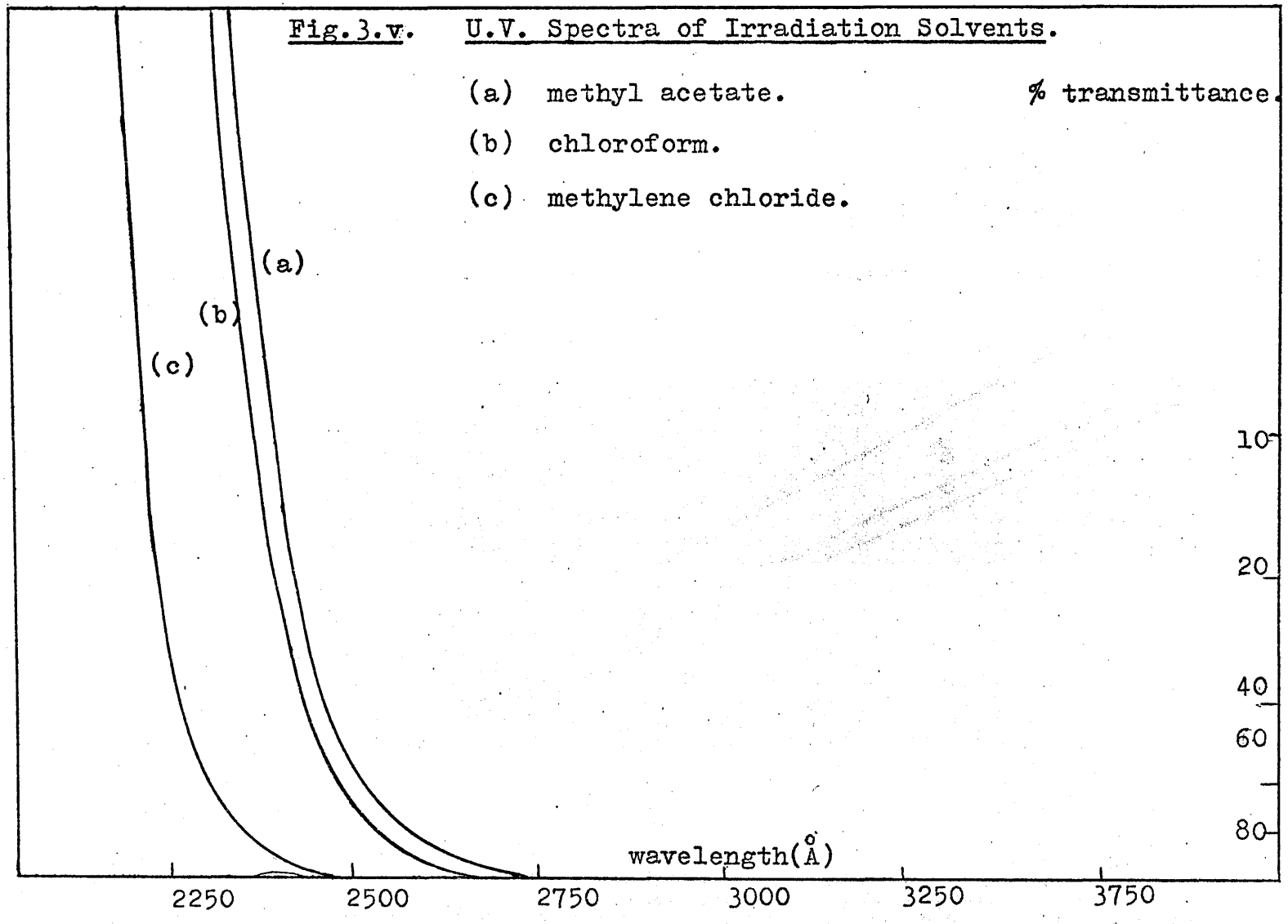


Fig.3.v. U.V. Spectra of Irradiation Solvents.
(a) methyl acetate.
(b) chloroform.
(c) methylene chloride.
% transmittance.
(a)
(b)
(c)
10
20
40
60
80
wavelength(Å)
2250
2500
2750
3000
3250
3750

Fig.3.vi. Irradiation of Poly-(Methyl Acrylate) in Different Solvents.

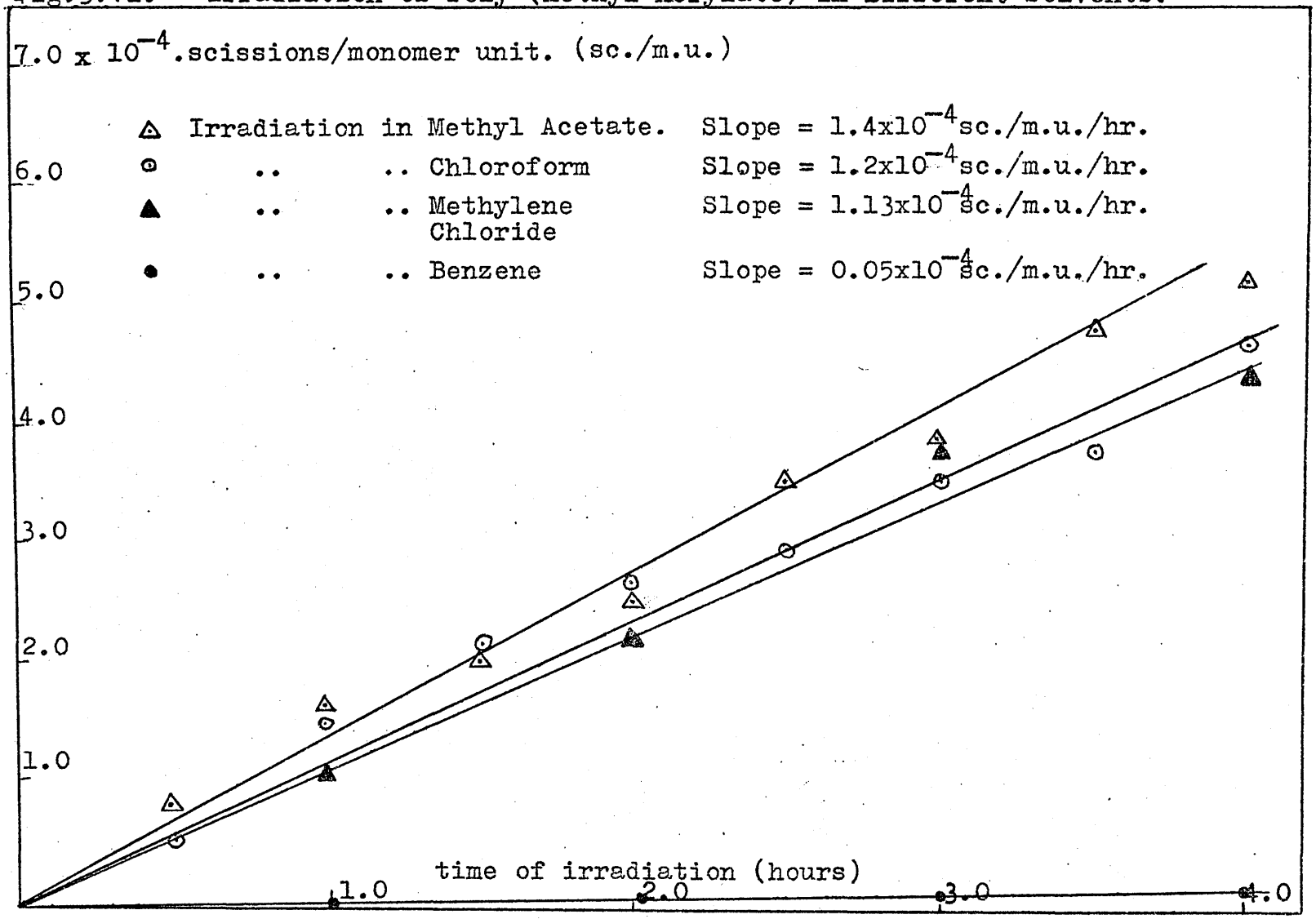


Fig.3.vii. 1% W/V PMA. in methyl acetate.

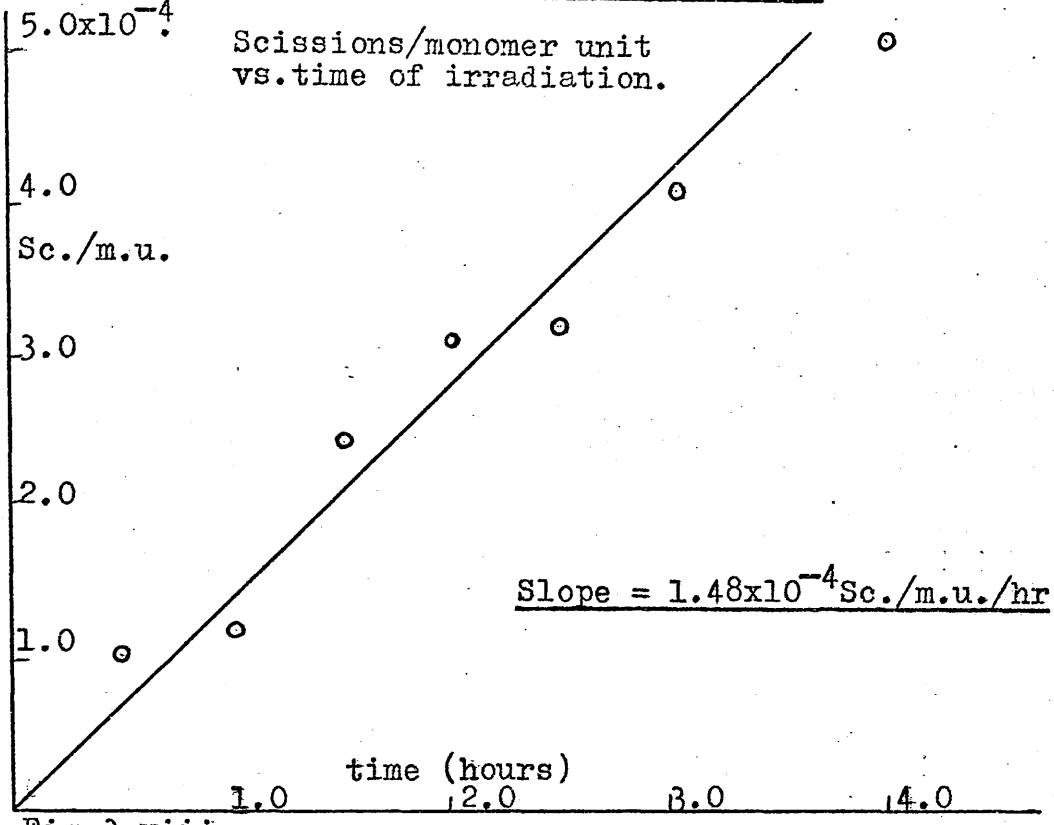


Fig.3.viii.

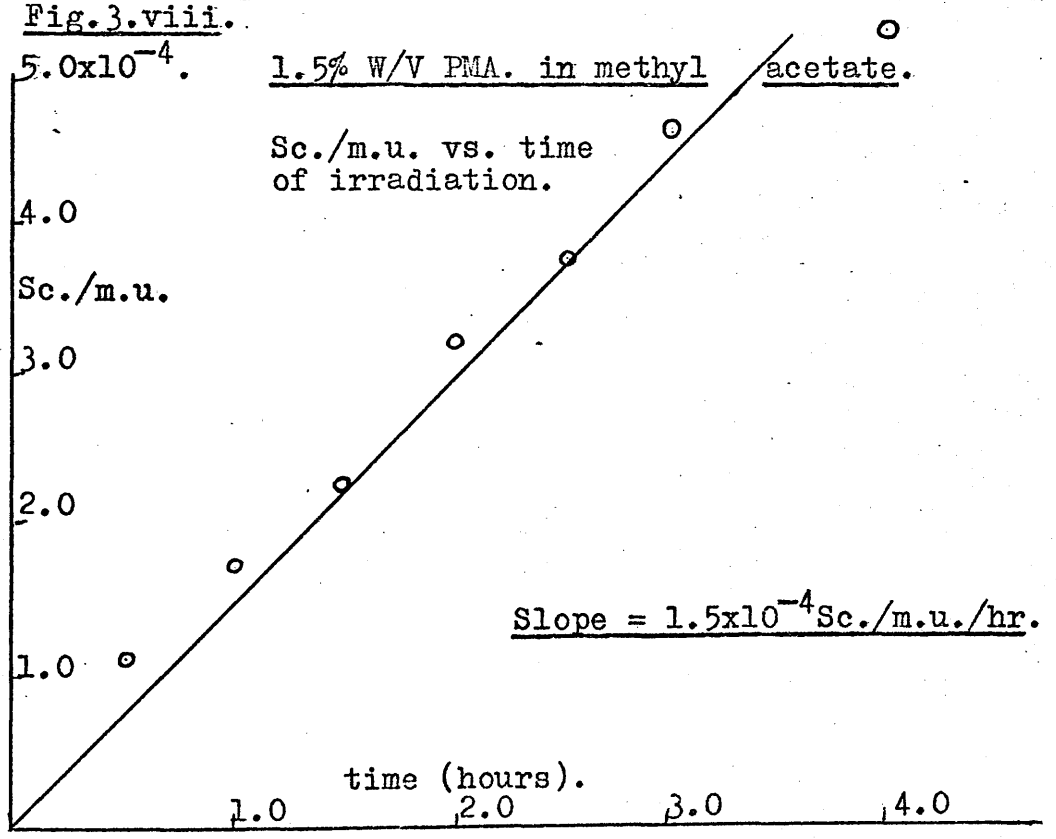


Fig.3.ix. 2.0% W/V PMA. in methyl acetate.

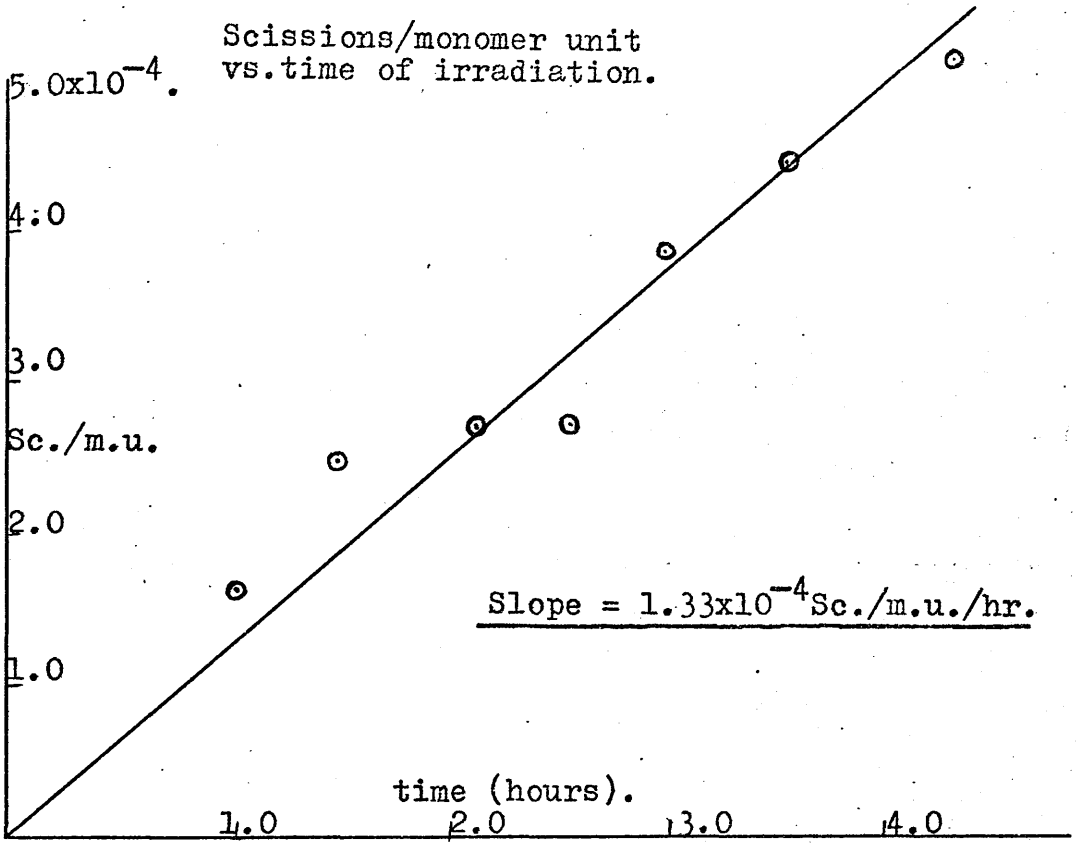


Fig.3.x. 5% W/V PMA. in methyl acetate.

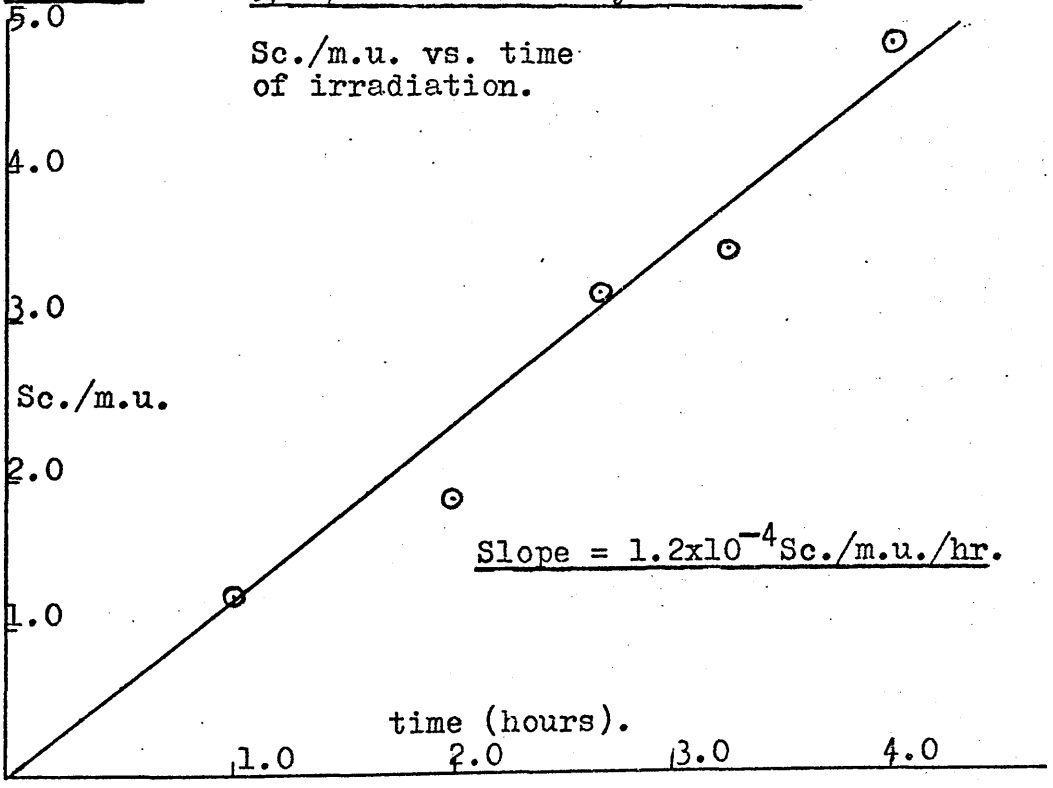


Fig.3.xi. 8% W/V PMA. in methyl acetate.

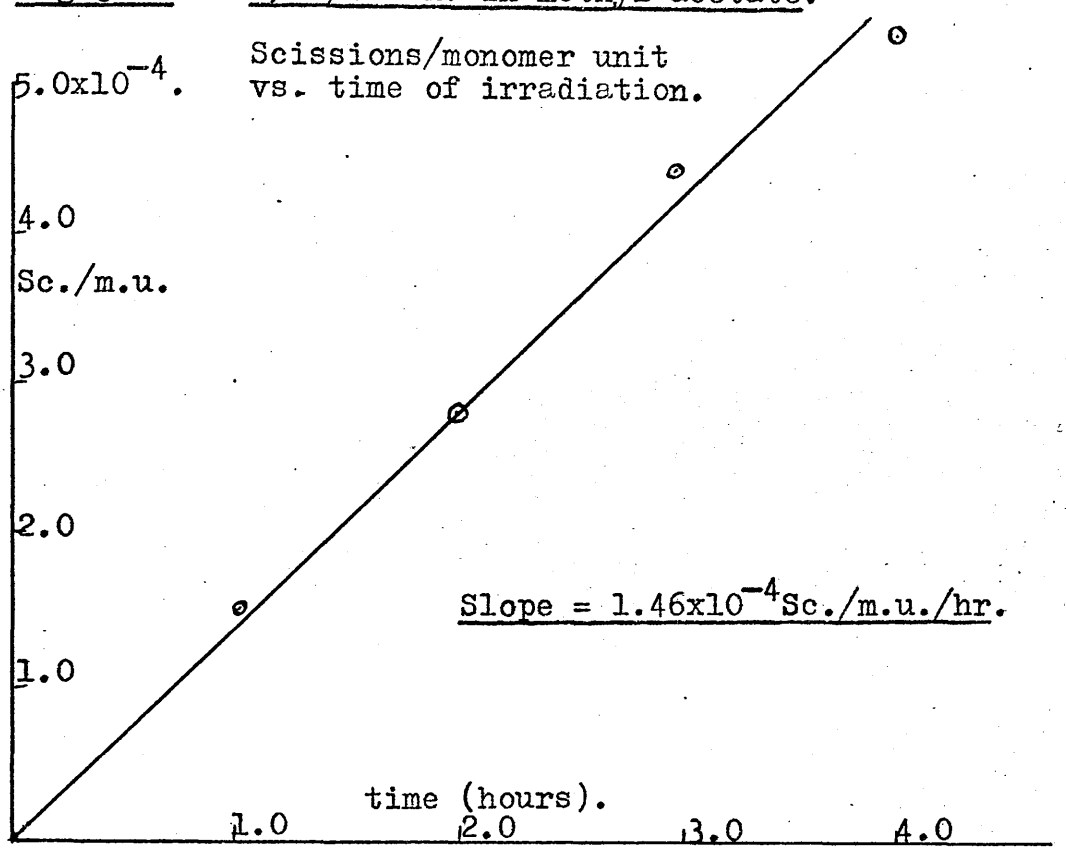


Fig.xii. 10% W/V PMA. in methyl acetate.

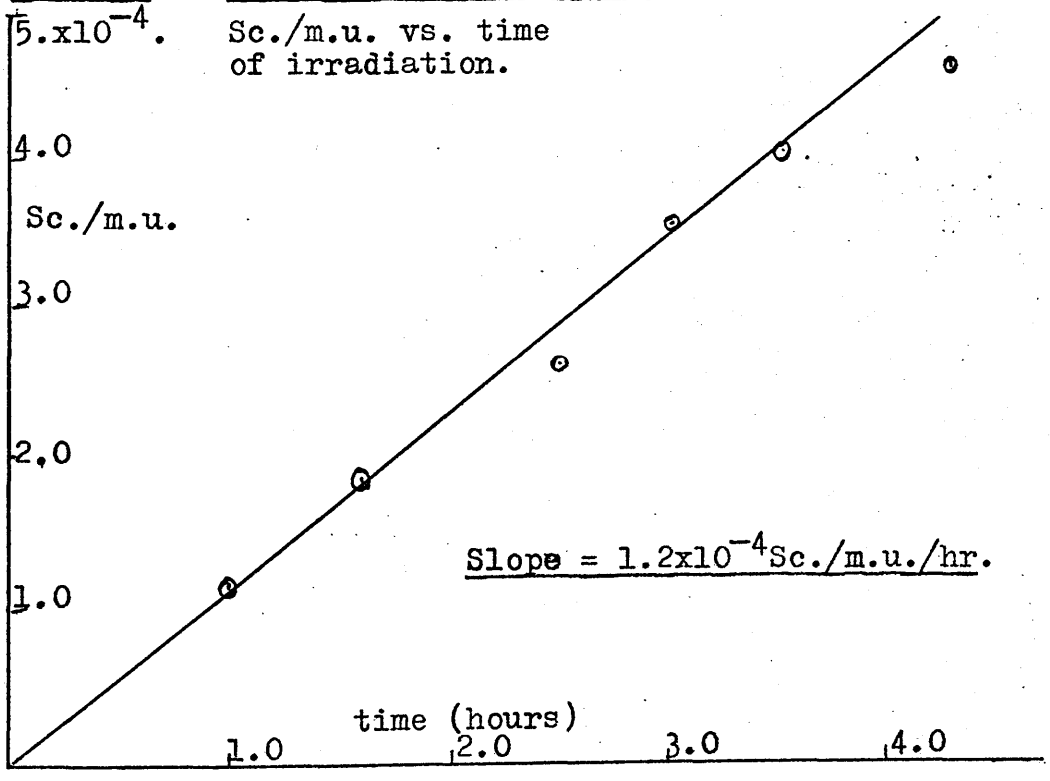


Fig.3.xiii. 1.0% W/V PMA. in chloroform.

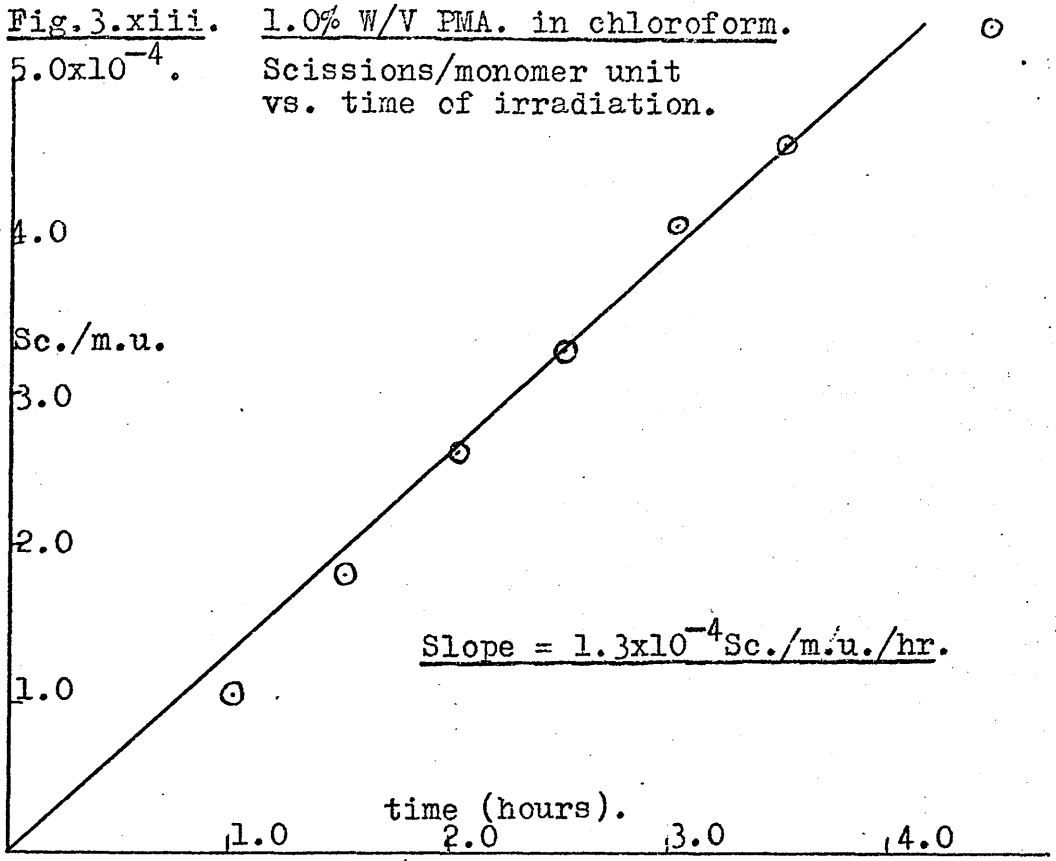


Fig.3.xiv. 1.5% W/V PMA. in chloroform.

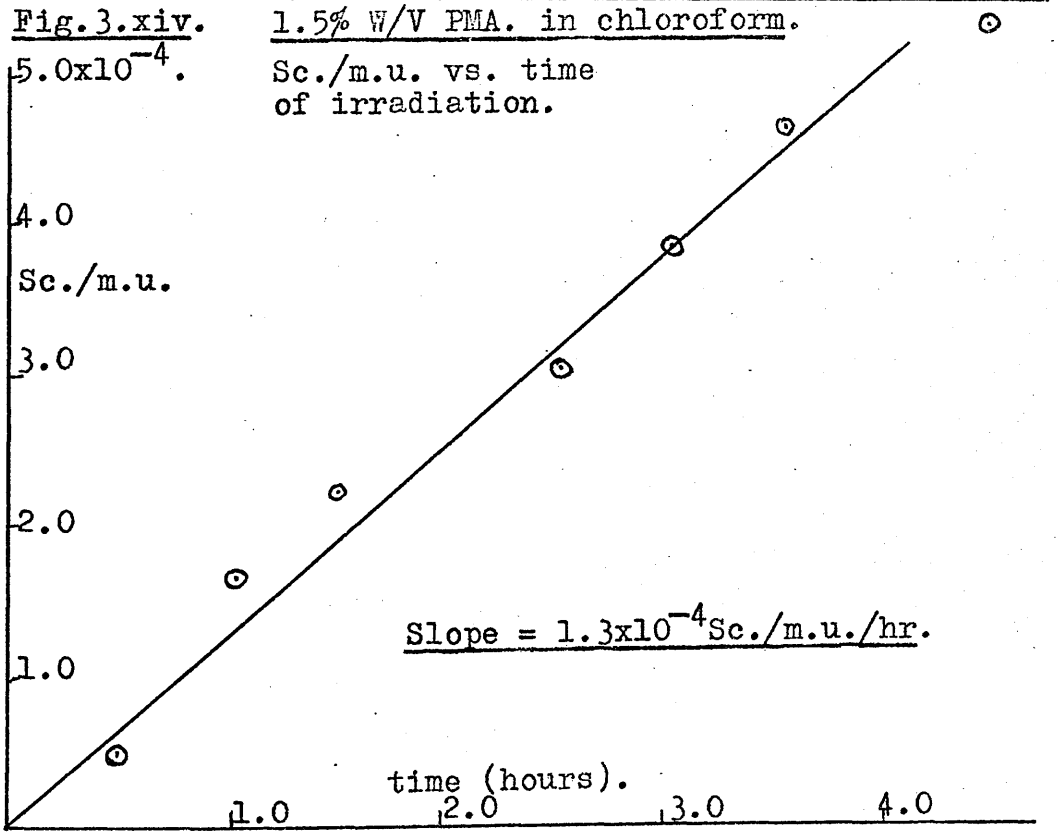


Fig. 3.xv. 2.0% W/V PMA. in chloroform.

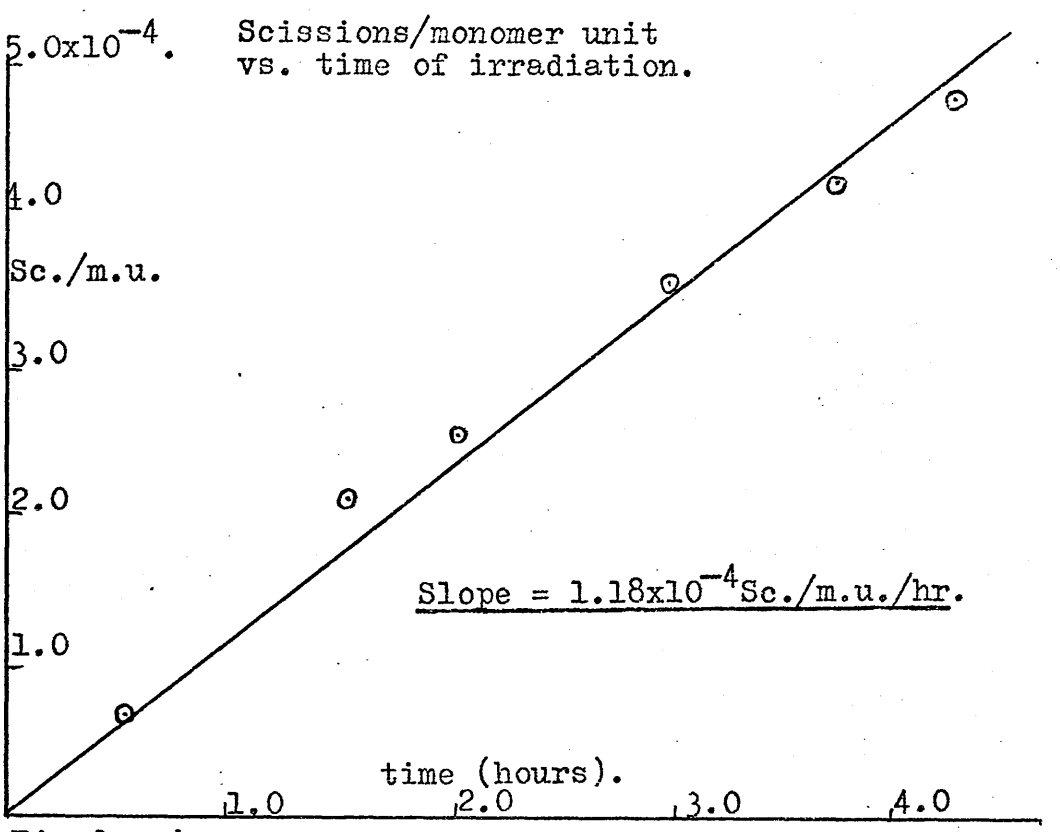


Fig.3.xvi. 2.5% W/V PMA. in chloroform.

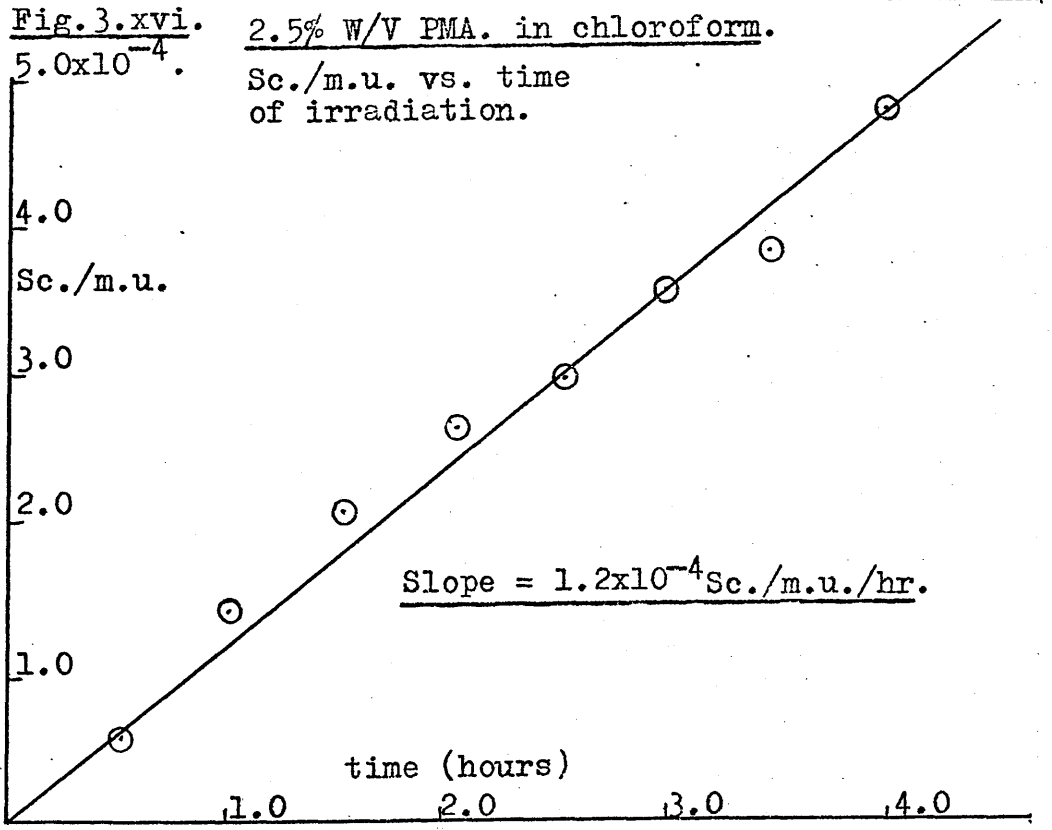


Fig.3.xvii. 9.0% W/V PMA. in chloroform.

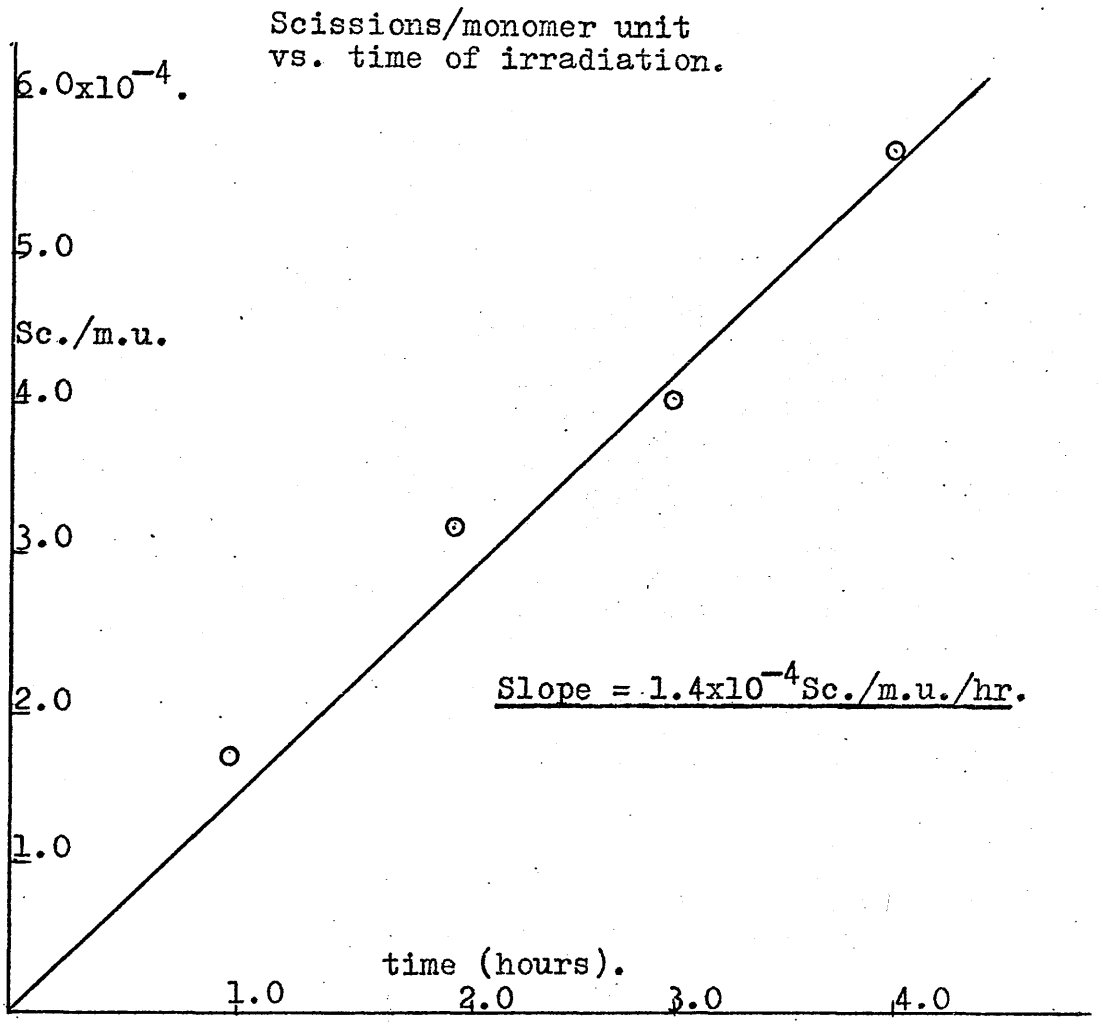


Fig.3.xviii. Rate of Chain Scission vs. PMA.Concentration

⊙ methyl acetate solutions.
× chloroform solutions.

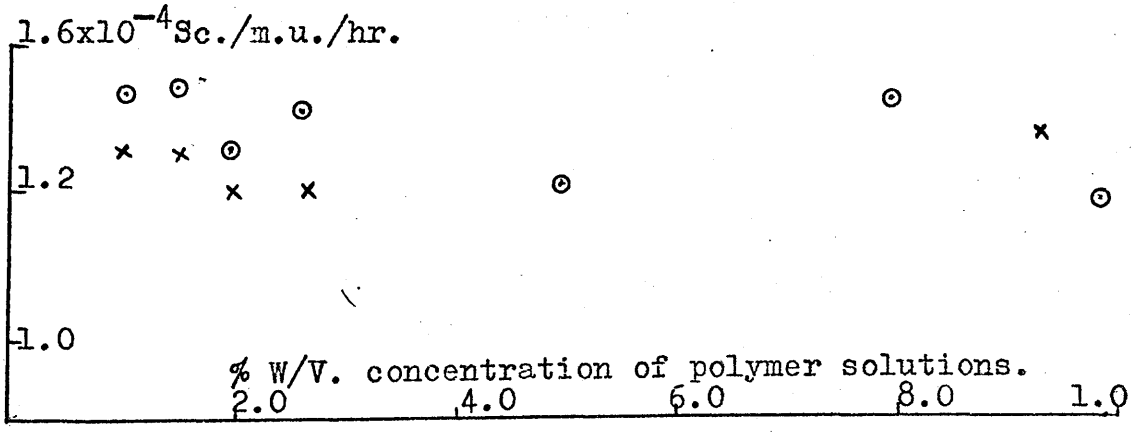


Fig.3.ixx. Solution of PMA.(2%W/V) and Azo-bis-isobutyronitrile (1%W/V) in Methyl Acrylate.

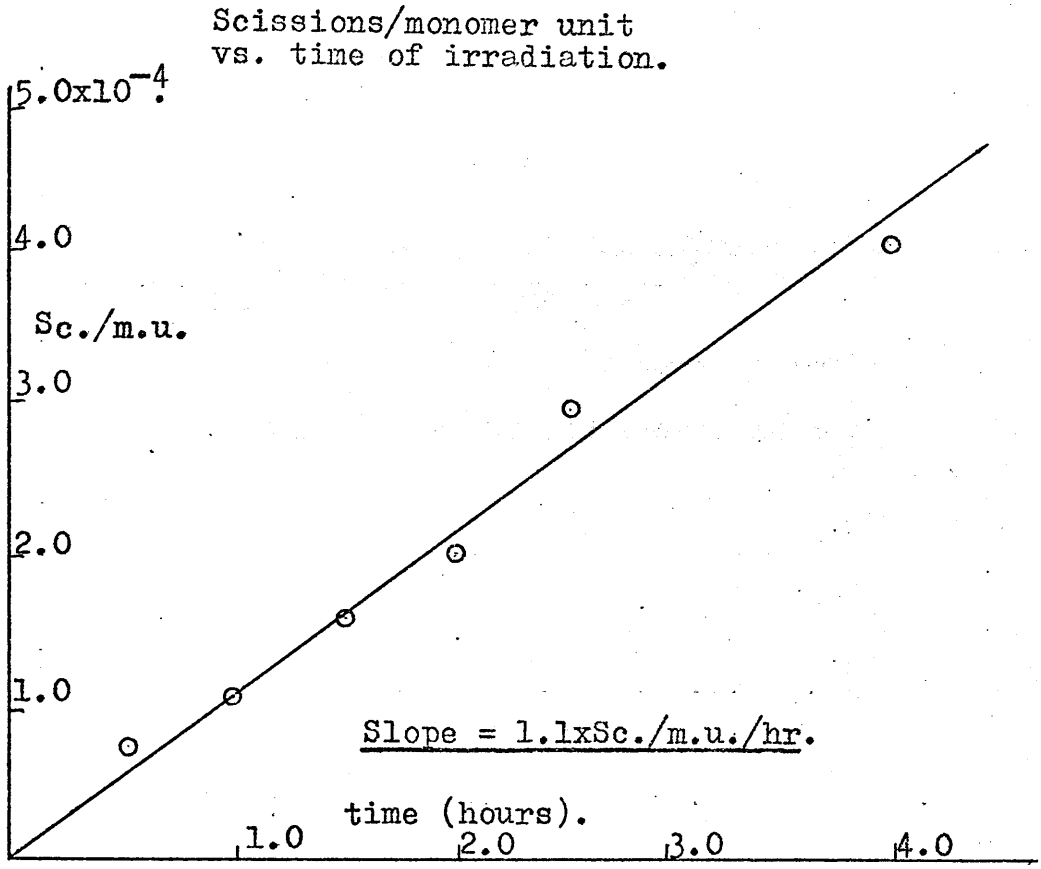
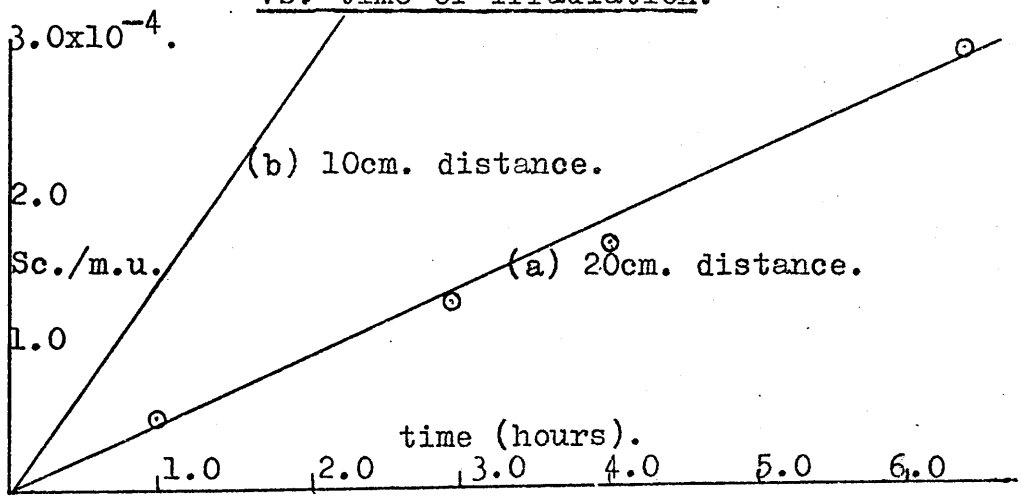


Fig.3.xx. Rate of Chain Scission vs. time of irradiation.



CHAPTER 4.

RESULTS.

4.1. Photolysis of Copolymers of Methyl Methacrylate and Methyl Acrylate.

For the study of copolymers of methyl methacrylate and methyl acrylate in solution, the solvent chosen was methyl acetate and solutions of 20mg./ml. concentration were prepared and irradiated as described in chapter 2. The molecular weight and calculated chain scission data obtained for each copolymer are tabulated in table 4.i. and these are shown graphically in figs. 4.i,ii,and iii. Similarly the molecular weight determinations resulting from the photolysis of this copolymer system in film form under a pressure of oxygen are listed in table 4.ii. and plotted in figs.4.iv,v,vi and vii. Photolysis data of the oxygenated polymer solutions are listed in table 4.iii. and plotted in figs.4viii—x.

For the purposes of reference fig.4xi,which summarises the degradation characteristics of these copolymers in thin film form[73] under vacuum has been included.

Spectroscopic Analysis.

The infra-red spectra of the copolymers were recorded before and after irradiation and compared. Apart from a slight broadening of the peaks in the carbonyl absorption region in the cases of photo-oxidation, no appreciable change was observed. Similarly the ultra-violet spectra of the irradiated polymers were almost identical to those of the unirradiated polymers.

4.2. Photolysis of Copolymers of Methyl Methacrylate with a. Maleic Anhydride and b. Methacrylonitrile.

a. Maleic Anhydride Copolymers.

As with the methyl acrylate copolymers, the photolysis of this copolymer system was carried using solutions in methyl acetate; photolysis cells of the type shown in fig. 2.i. were used. The results of the molecular weight determinations are shown in table 4.iv, which also shows the calculated chain scission data which are plotted in figs.4.xii — xiv. As in studies of the methyl methacrylate/methyl acrylate copolymer system, no infra-red or ultra-violet spectroscopic evidence of degradation was observed.

b. Methacrylonitrile Copolymers.

Samples of this copolymer system were irradiated

in solutions of methylene chloride (20mg./ml.). Molecular weight and chain scission data are presented in table 4.v. and plotted in figs.4.xv—xvii. Because of the insolubility of these copolymers in toluene, the molecular weight determinations were carried out in cyclohexanone solution. Some of the osmometer data obtained showed more scatter than is usual for this technique. However, by drawing the best straight line of gradient equal to that of the osmometry plot for the starting polymers, satisfactory molecular weight determinations were obtained. In this case also, no spectroscopic evidence of degradation was observed.

4.3. Photolysis of Copolymers of Methyl Methacrylate and Styrene.

The two homopolymers of styrene and methyl methacrylate and a series of copolymers covering the whole composition range were irradiated in solution in methylene chlorideusing the apparatus shown in fig.2.vii.

The details of the molecular weight analyses of this system are presented in table 4.vi, and the plots of chain scission versus time of irradiation are shown in figs. 4.xviii — 4.xx. From the slopes of these graphs the rates of chain scission of the polymers were

obtained and these, plotted against copolymer composition, are illustrated in fig.4.xxi. It must be noted here that the apparatus used in this work is different from that employed in other solution studies and for this reason the rate of chain scission of the homopolymer of methyl methacrylate is different to that given earlier.

b. Ultra-violet Spectra.

The ultra-violet spectra of the homopolymers and the copolymers were recorded before irradiation and these are illustrated in fig.4.xxii. From these spectra the absorbance of each polymer at a wavelength of 2537Å was read off and converted to transmittance. The transmittance values at this wavelength plotted against copolymer composition are shown in fig.4.xxiii. The ultra-violet spectra of the degraded solutions showed little change except for a slight general increase in absorbance in the region 4000-2750Å. An exception to this was observed in the long irradiation of the solution of polystyrene homopolymer which showed a strong general increase in absorbance in this region, as shown in fig.4xxiv. In this case, the solution had a pronounced yellow coloration after 14 hours degradation and the same phenomenon was observed on repetition of this long - period irradiation.

4.4. Coloration of Polystyrene.

a. Solutions.

Solutions of polystyrene in methylene chloride which were irradiated for more than five hours became progressively yellow and the ultra-violet spectra showed a progressive and general increase in absorption in the region 4000Å – 2000Å (fig.xxv). Similar long irradiations of the range of copolymers of this system in the same solvent yielded comparable results. Although the ultra-violet spectra showed good evidence of spectroscopic change in the system, no change in the infra-red spectra was observed.

Similar irradiations of polystyrene in solutions of chloroform and chloroethane produced the same coloration and the ultra-violet spectra were similar to that in fig.xxiv.

Irradiation of polystyrene in solutions of methyl acetate and cyclohexane showed no evidence of coloration and no change in the ultra-violet spectra.

The solvents, methylene chloride, chloroform, chloroethane, methyl acetate and cyclohexane were themselves irradiated in the same apparatus as used for the polymer solutions. After equal lengths of time of irrad-

iation, their ultra-violet spectra were recorded. The spectra of methyl acetate and cyclohexane showed no change but those of the other three solvents showed a large general increase in absorption over the region 4000 – 2250Å similar to that shown in fig.xxv.

b. Polystyrene Films.

These were prepared as described in chapter 2.4.b. Several 12 hour irradiations were carried out and they all resulted in coloration of the type observed in the irradiation of the polymer solutions. The ultra-violet spectra of the irradiated films also showed similar changes to those observed in the solution irradiations. Additional polymer films from which all residual chloroform had been removed as described in chapter 2.4.c. were irradiated for similar periods of time and compared. It was found that these films showed no visible coloration, nor did they show any appreciable change in their ultra-violet spectra.

c. Thermal Volatilisation Analysis.[74]

Thermal volatilisation analysis of the polystyrene films prepared as sections 2.4.b. and 2.4.c. was carried out. The thermograms of films prepared by the former

procedure contained a small peak corresponding to a commencement of volatilisation at 116°C whereas this peak was totally absent in the thermograms for the films prepared by the latter method. This peak was attributed to volatilisation of residual chloroform, which was absent in the films purified by the more stringent method employing heating under vacuum at temperatures close to the melting point of polystyrene. This confirmed that all of the chloroform had been removed as suggested by the reading on the Pirani Vacuum Gauge as heating progressed. Otherwise, all characteristics of the two thermograms were identical, indicating that the purification procedure had not altered the chemical characteristics of the films in any way.

Table 4.i.

Irradiation of Copolymers of Methyl Methacrylate(MMA.) and Methyl Acrylate(MA.) in Methyl Acetate.

Copolymer composition.	Time(hours) of irradiation.	Molecular weight.	Scissions/ monomer unit.
100% MA.	–	–	see fig. 3.xviii
90% MA.	1.0	226,000	1.38×10^{-4}
	2.0	198,000	1.93×10^{-4}
	3.0	164,000	2.83×10^{-4}
	4.0	140,000	3.75×10^{-4}
70%MA.	1.0	200,000	0.75×10^{-4}
	2.0	174,000	1.39×10^{-4}
	3.0	152,000	2.26×10^{-4}
	4.0	140,000	2.7×10^{-4}
50% MA.	1.0	185,000	1.0×10^{-4}
	2.0	136,000	2.76×10^{-4}
	3.0	125,000	3.36×10^{-4}
	4.0	104,000	4.8×10^{-4}
30% MA.	1.0	140,000	3.42×10^{-4}
	2.0	98,000	6.2×10^{-4}
	3.0	75,000	9.0×10^{-4}
	4.0	65,000	10.8×10^{-4}

Table 4.i. (continued)

Copolymer composition.	Time(hours) of irradiation.	Molecular weight.	Scissions/ monomer unit.
15% MA.	0.5	282,000	1.79×10^{-4}
	1.0	190,000	3.6×10^{-4}
	2.0	125,000	6.4×10^{-4}
	2.5	97,000	8.7×10^{-4}
	3.5	77,000	11.5×10^{-4}
	4.0	70,000	12.7×10^{-4}
100% MMA.	0.5	180,000	2.57×10^{-4}
	1.0	115,000	6.0×10^{-4}
	1.25	95,000	7.85×10^{-4}
	2.33	57,000	14.9×10^{-4}
	3.0	49,000	17.7×10^{-4}
	4.0	40,000	22.3×10^{-4}

Table 4.ii.

Photo-oxidation of Films of Copolymers of Methyl Methacrylate and Methyl Acrylate.

Copolymer composition.	Time(hours) of irradiation.	Molecular weight.	Scissions/ monomer unit.
100%MMA.	0.5	320,000	0.43×10^{-4}
	1.0	270,000	1.0×10^{-4}
	1.5	250,000	1.3×10^{-4}
	2.0	221,000	1.84×10^{-4}
15%MA.	0.5	340,000	1.1×10^{-4}
	1.0	240,000	2.3×10^{-4}
	1.5	210,000	2.95×10^{-4}
	2.0	170,000	4.0×10^{-4}
50%MA.	0.5	294,000	1.35×10^{-4}
	1.0	202,000	2.75×10^{-4}
	1.5	170,000	4.0×10^{-4}
	2.0	128,000	5.4×10^{-4}
70%MA.	0.5	210,000	1.61×10^{-4}
	1.0	170,000	2.67×10^{-4}
	1.5	128,000	4.45×10^{-4}
	2.0	110,000	4.95×10^{-4}

Table 4.ii. (continued).

Copolymer composition.	Time(hours) of irradiation.	Molecular weight.	Scissions/ monomer unit.
89% MA.	0.5	230,000	1.34×10^{-4}
	1.0	167,000	2.8×10^{-4}
	1.5	144,000	3.66×10^{-4}
	2.0	120,000	5.1×10^{-4}
100% MA.	0.5	238,000	1.21×10^{-4}
	1.0	176,000	2.50×10^{-4}
	1.5	147,000	3.40×10^{-4}
	2.0	118,000	4.85×10^{-4}

Table 4.iii. Photo-oxidation of Copolymers of Methyl Methacrylate and Methyl Acrylate in Methyl Acetate.

Polymer composition.	Time(hours) of irradiation.	Molecular weight.	Scissions/ monomer unit.
100%MMA.	0.5	204,000	2.2×10^{-4}
	1.0	192,000	2.5×10^{-4}
	1.5	121,000	5.55×10^{-4}
	2.0	106,000	6.75×10^{-4}
15%MA.	0.5	214,000	2.84×10^{-4}
	1.0	139,000	5.26×10^{-4}
	1.5	111,000	7.04×10^{-4}
	2.0	88,000	9.35×10^{-4}
50%MA.	0.5	154,000	2.33×10^{-4}
	1.0	137,000	3.08×10^{-4}
	1.5	100,000	5.6×10^{-4}
	2.0	83,000	7.45×10^{-4}
70%MA.	0.5	152,000	2.2×10^{-4}
	1.0	128,000	3.31×10^{-4}
	1.5	105,000	4.87×10^{-4}
	2.0	93,000	6.0×10^{-4}
90%MA.	0.5	230,000	1.4×10^{-4}
	1.0	148,000	3.54×10^{-4}
	1.5	110,000	5.6×10^{-4}
	2.0	95,000	6.9×10^{-4}
100%MA.	0.5	193,000	2.06×10^{-4}
	1.0	159,000	3.01×10^{-4}
	1.5	133,000	4.06×10^{-4}
	2.0	100,000	5.55×10^{-4}

Table 4. iv.

Irradiation of Copolymers of Methyl Methacrylate (MMA) and Maleic Anhydride.

Polymer composition.	Time(hours) of irradiation.	Molecular weight.	Scissions/ monomer unit.
100%MMA.	0.5	169,000	3.22×10^{-4}
	1.0	120,000	5.64×10^{-4}
	1.5	85,000	9.05×10^{-4}
	2.0	81,000	10.2×10^{-4}
98.4%MMA.	0.5	127,000	$4,96 \times 10^{-4}$
	1.0	92,000	8.0×10^{-4}
	1.5	65,000	12.5×10^{-4}
	2.0	50,000	17.1×10^{-4}
97%MMA.	0.5	147,000	4.48×10^{-4}
	1.0	90,000	8.80×10^{-4}
	1.5	65,000	13.2×10^{-4}
	2.0	49,300	17.7×10^{-4}
93.8%MMA.	0.5	103,000	5.55×10^{-4}
	1.0	65,000	11.2×10^{-4}
	1.5	44,000	18.5×10^{-4}
	2.0	36,000	23.6×10^{-4}
93.2%MMA	0.75	49,000	12.2×10^{-4}
	1.5	36,300	19.4×10^{-4}
	2.0	27,300	28.4×10^{-4}
	3.0	19,700	42.5×10^{-4}

Table 4.v.

Irradiation of Copolymers of Methyl Methacrylate and Methacrylonitrile (MAN.)

Polymer composition.	Time(hours) of irradiation.	Molecular weight.	Scissions/ monomer unit
88%MAN.	0.5	82,400	1.2×10^{-4}
	1.0	54,700	5.5×10^{-4}
	1.5	47,000	7.58×10^{-4}
	2.0	42,000	9.74×10^{-4}
79%MAN.	0.5	76,000	1.94×10^{-4}
	1.0	67,000	3.24×10^{-4}
	1.5	66,000	3.41×10^{-4}
	2.0	54,000	5.89×10^{-4}
62%MAN	0.5	121,000	2.36×10^{-4}
	1.0	80,600	5.5×10^{-4}
	1.5	65,000	8.1×10^{-4}
	2.0	55,600	10.1×10^{-4}
54%MAN	0.5	68,000	4.63×10^{-4}
	1.0	51,500	8.44×10^{-4}
	1.5	40,000	13.3×10^{-4}
	2.0	34,000	14.9×10^{-4}

Table 4.v. (continued).

Polymer composition.	Time(hours) of irradiation.	Molecular weight.	Scissions/ monomer unit.
35 %MAN.	0.5	59,000	6.03×10^{-4}
	1.0	53,000	7.75×10^{-4}
	1.5	37,000	15.1×10^{-4}
	2.0	30,000	20.7×10^{-4}
23 %MAN	0.5	77,000	2.88×10^{-4}
	1.0	52,500	8.55×10^{-4}
	1.5	48,000	10.2×10^{-4}
	2.0	39,000	15.6×10^{-4}
12 %MAN.	0.5	82,000	5.35×10^{-4}
	1.0	60,300	9.42×10^{-4}
	1.5	46,000	14.6×10^{-4}
	2.0	40,000	17.7×10^{-4}
100MMA.	See table 4.i.		

Table 4.vi.

Irradiation of Copolymers of Methyl Methacrylate and Styrene.

Polymer composition.	Time(hours) of irradiation.	Molecular weight.	Scission/ monomer unit.
100%MMA.	0.5	150,000	4.03×10^{-4}
	1.0	91,000	8.35×10^{-4}
	1.5	68,000	12.1×10^{-4}
	2.0	51,000	16.8×10^{-4}
10%Styrene	0.75	196,000	1.77×10^{-4}
	1.50	146,000	3.50×10^{-4}
	2.25	120,000	5.0×10^{-4}
	3.25	90,000	7.77×10^{-4}
20%Styrene	0.75	175,000	1.68×10^{-4}
	1.50	164,000	2.12×10^{-4}
	2.25	120,000	3.04×10^{-4}
	3.25	90,000	5.1×10^{-4}
40%Styrene	0.75	235,000	0.15×10^{-4}
	1.50	209,000	0.29×10^{-4}
	2.25	189,000	0.43×10^{-4}
	3.0	170,000	0.58×10^{-4}

Table 4.vi.(continued).

Irradiation of Copolymers of MMA. and Styrene.

Polymer composition.	Time(hours) of irradiation.	Molecular weight.	Scissions/ monomer unit.
60% Styrene	2.0	210,000	0.92×10^{-4}
	3.0	185,000	1.55×10^{-4}
	4.5	164,000	2.24×10^{-4}
	5.0	162,000	2.32×10^{-4}
80% Styrene	2.0	210,000	0.76×10^{-4}
	3.0	195,000	1.13×10^{-4}
	4.0	182,000	1.56×10^{-4}
	5.0	170,000	1.88×10^{-4}
90%Styrene.	2.0	265,000	0.2×10^{-4}
	3.0	252,000	0.39×10^{-4}
	4.0	245,000	0.50×10^{-4}
	5.0	240,000	0.62×10^{-4}
100%Styrene.	14.0	230,000	— —

Fig. 4.i.

Irradiation of Copolymers of Methyl Methacrylate and Methyl Acrylate.

Scissions/monomer unit vs. irradiation time.

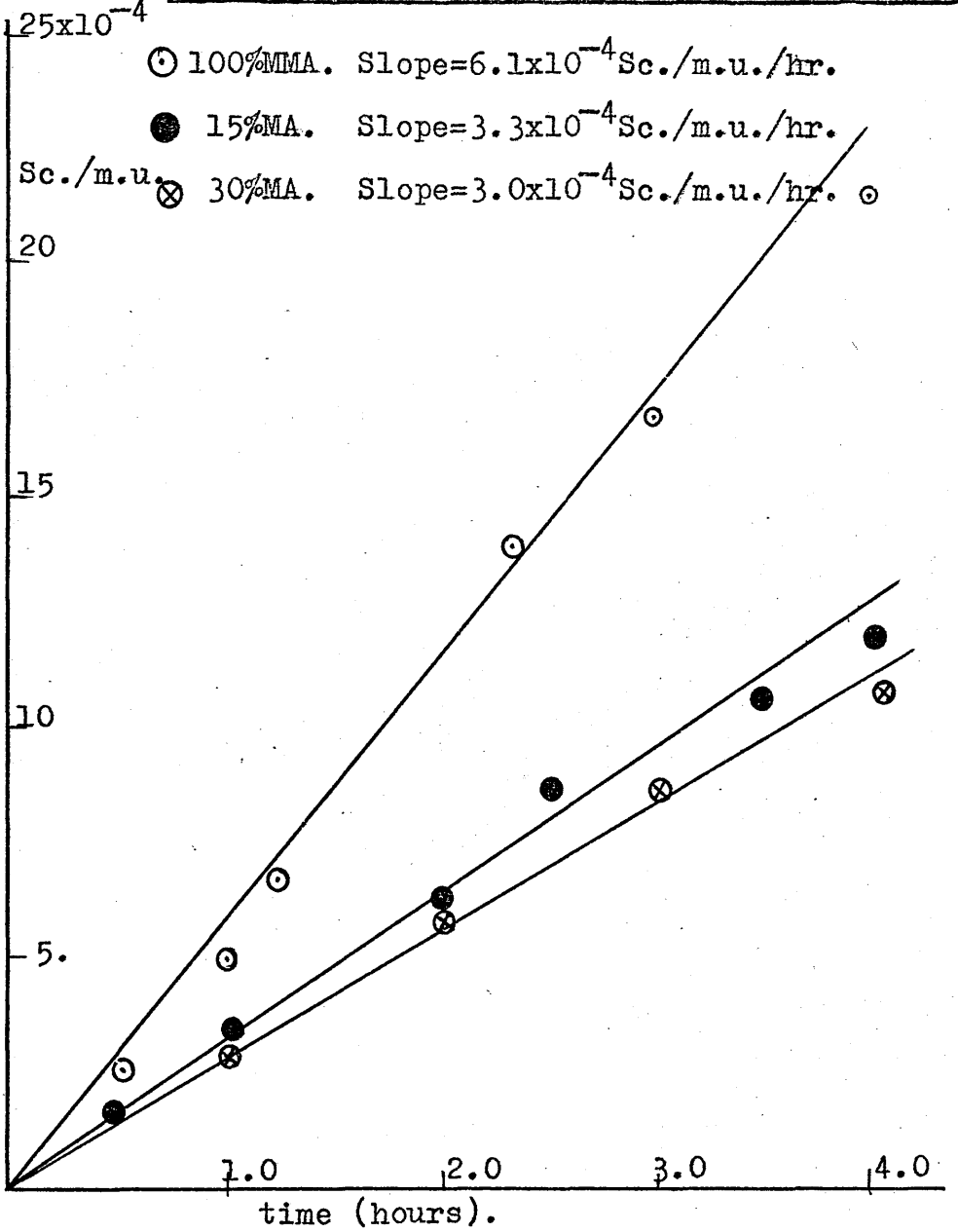


Fig.4.ii. Irradiation of Copolymers of MMA. and MA.

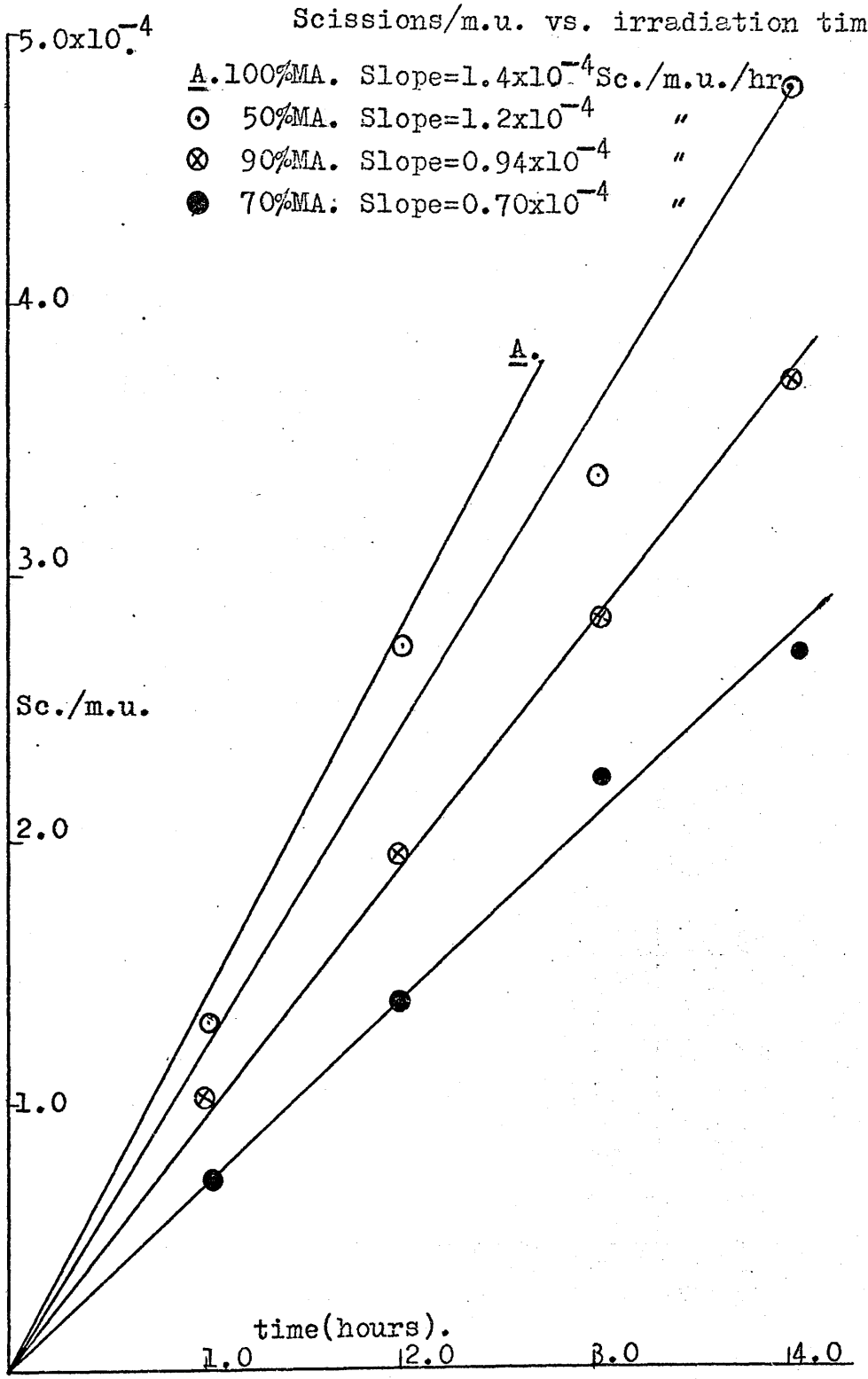


Fig. 4.iii.

Rate of chain scission vs. copolymer composition.
Copolymers of MMA. and MA.

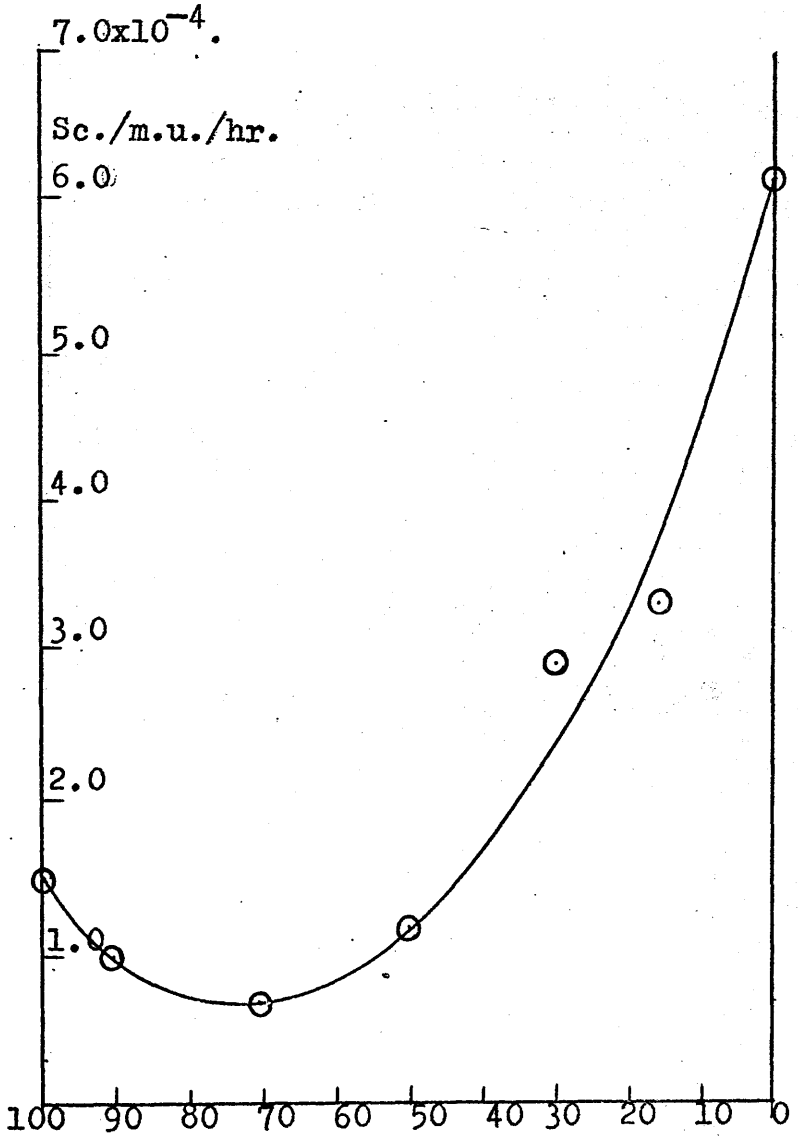


Fig. 4.iv.

Photo-oxidation of Copolymers of MMA and MA.

Scissions/monomer unit vs irradiation time.

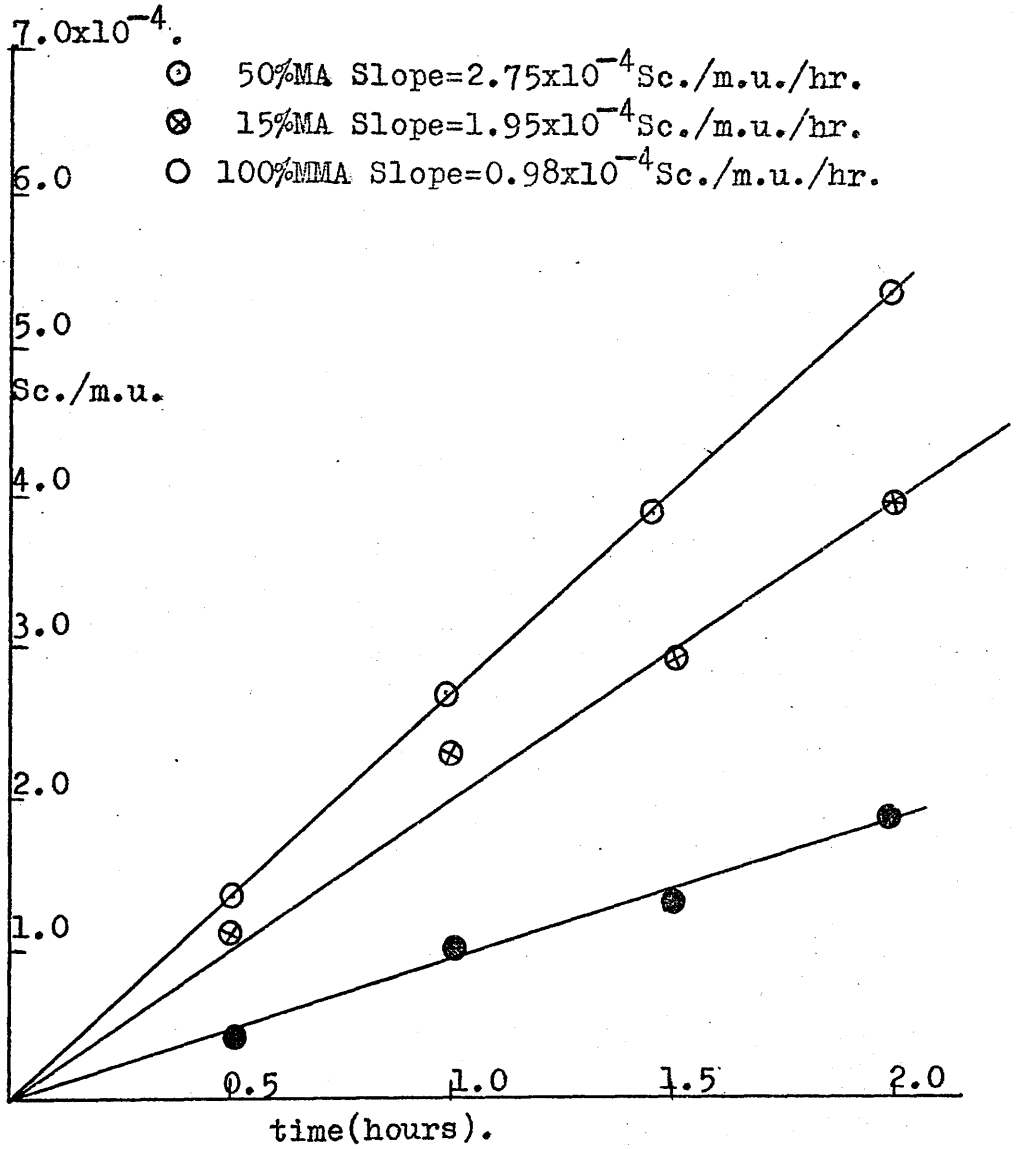


Fig. 4.v.

Photo-oxidation of Copolymers of MMA and MA:
Scissions/monomer unit vs irradiation time.

90% MA. Slope=2.6×10^{-4} Sc./m.u./hr.

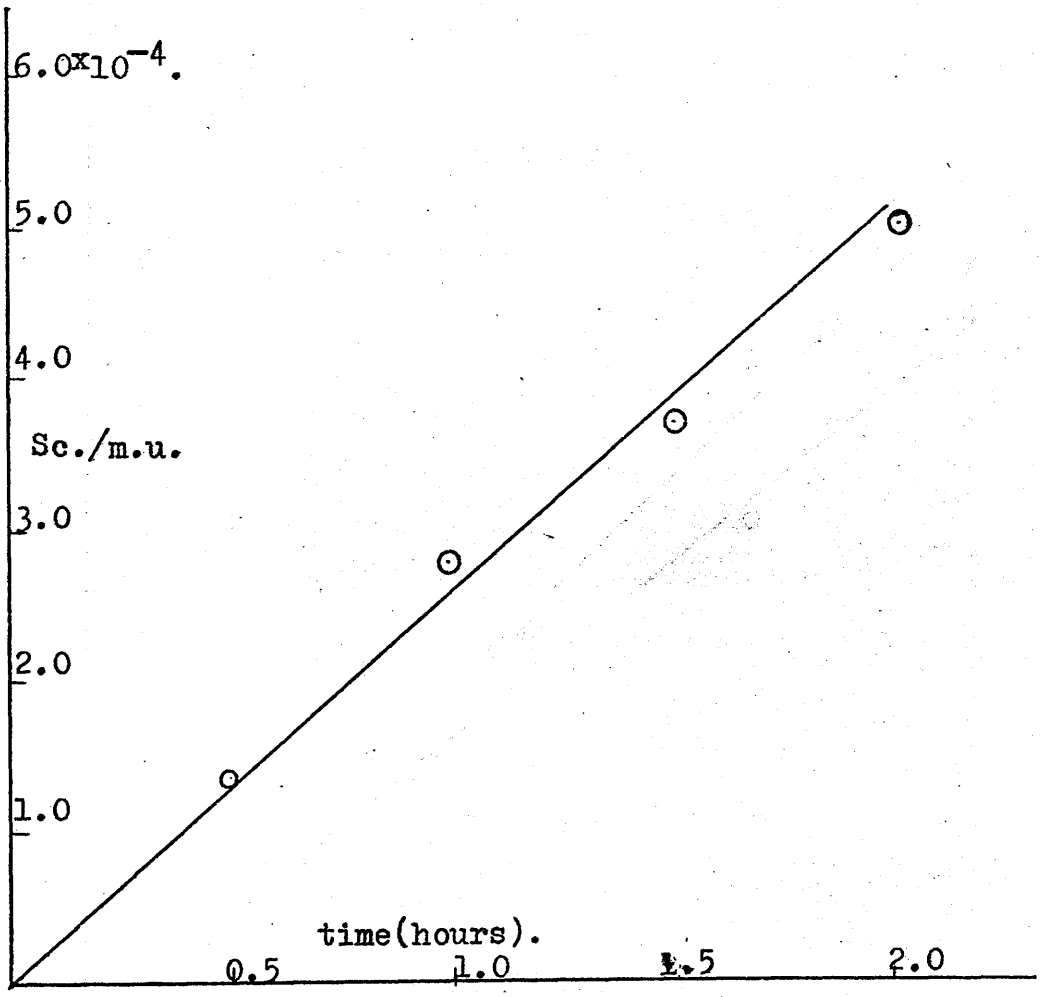


Fig. 4.vi.

Photo-oxidation of Copolymers of MMA and MA.

Scissions/monomer unit vs. irradiation time.

70% MA Slope=2.8×10^{-4}Sc./m.u./hr.

100% MA Slope=2.4×10^{-4}Sc./m.u./hr.

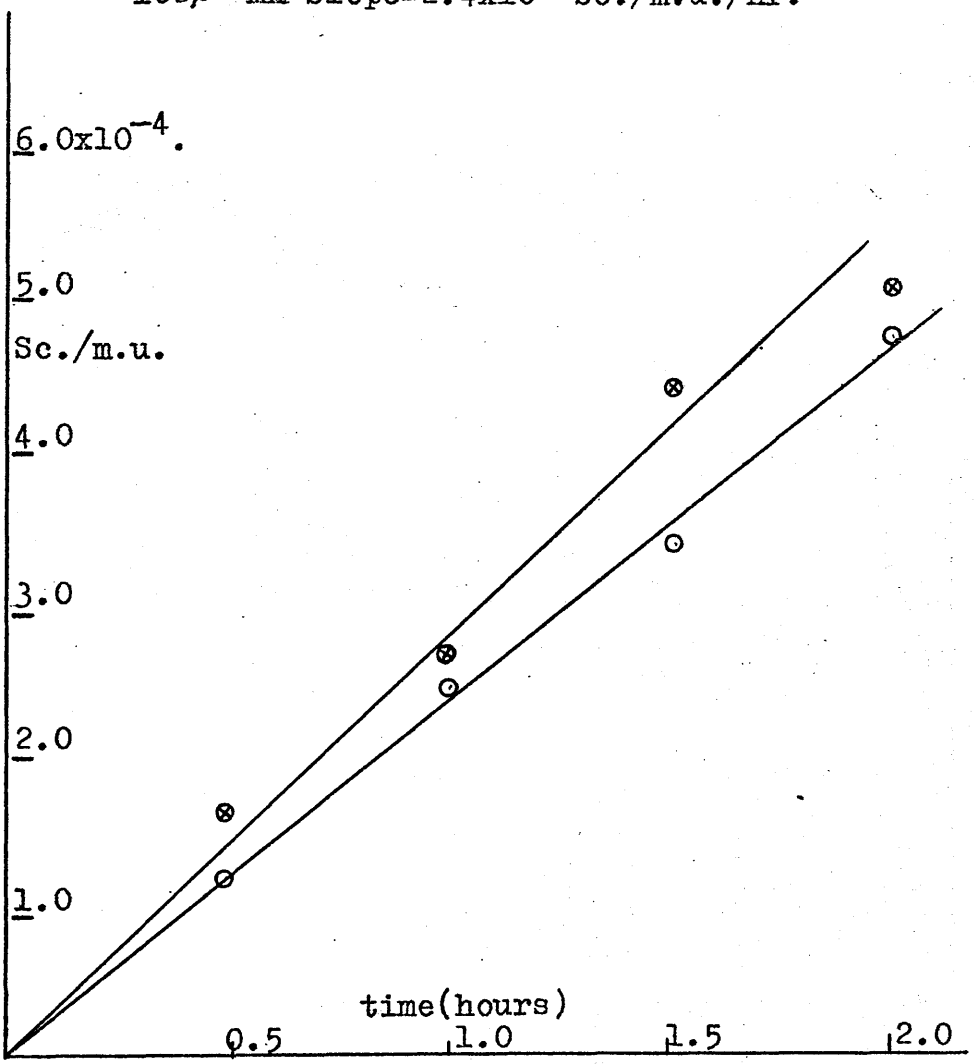


Fig.4.vii.

Photo-oxidation of Copolymers of MMA and MA.

Rate of chain scission vs. copolymer composition.

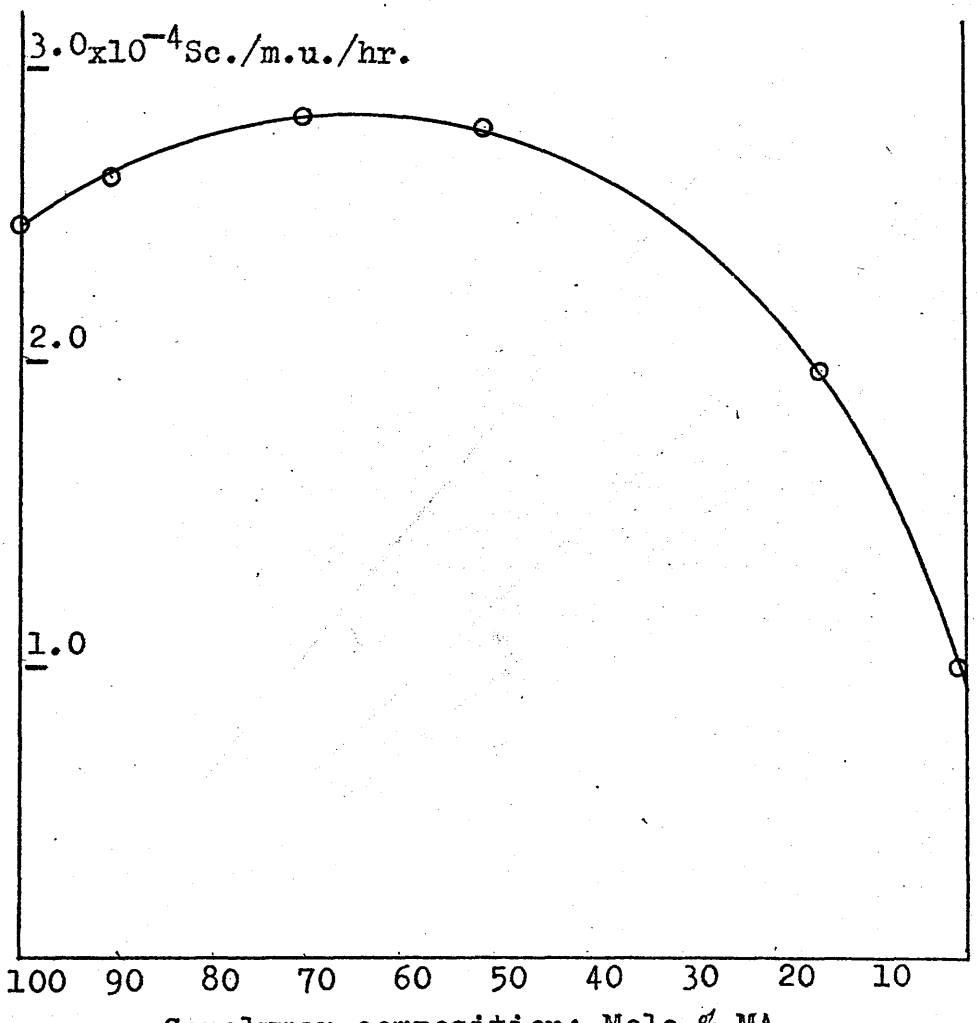


Fig.4viii Photo-oxidation of Copolymers of Methyl Methacrylate and Methyl Acrylate in Methyl Acetate.

Sc./m.u. vs. time of irradiation.

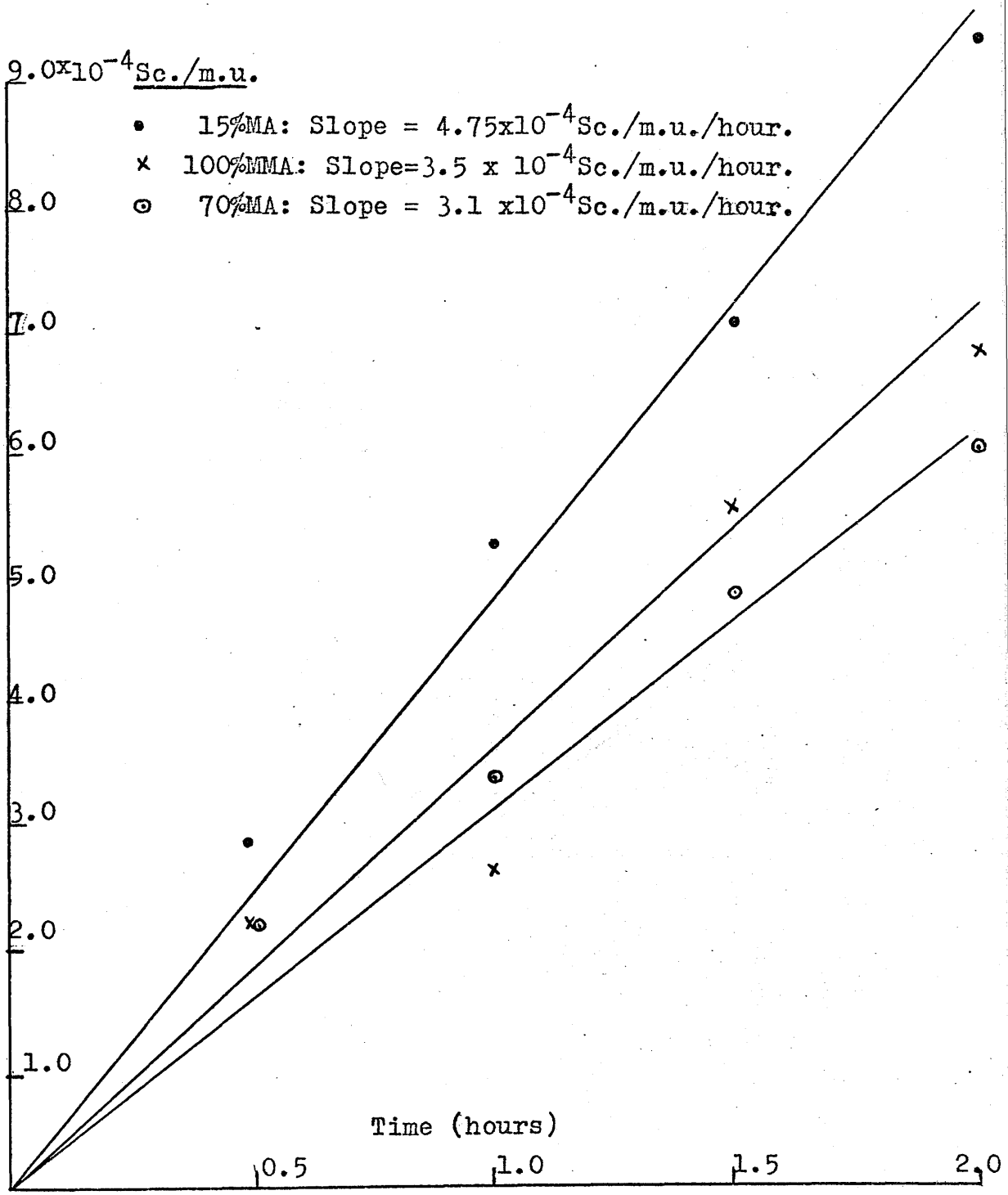


Fig. 4.ix. Photo-oxidation of Copolymers of Methyl Methacrate and Methyl Acrylate in Methyl Acetate.

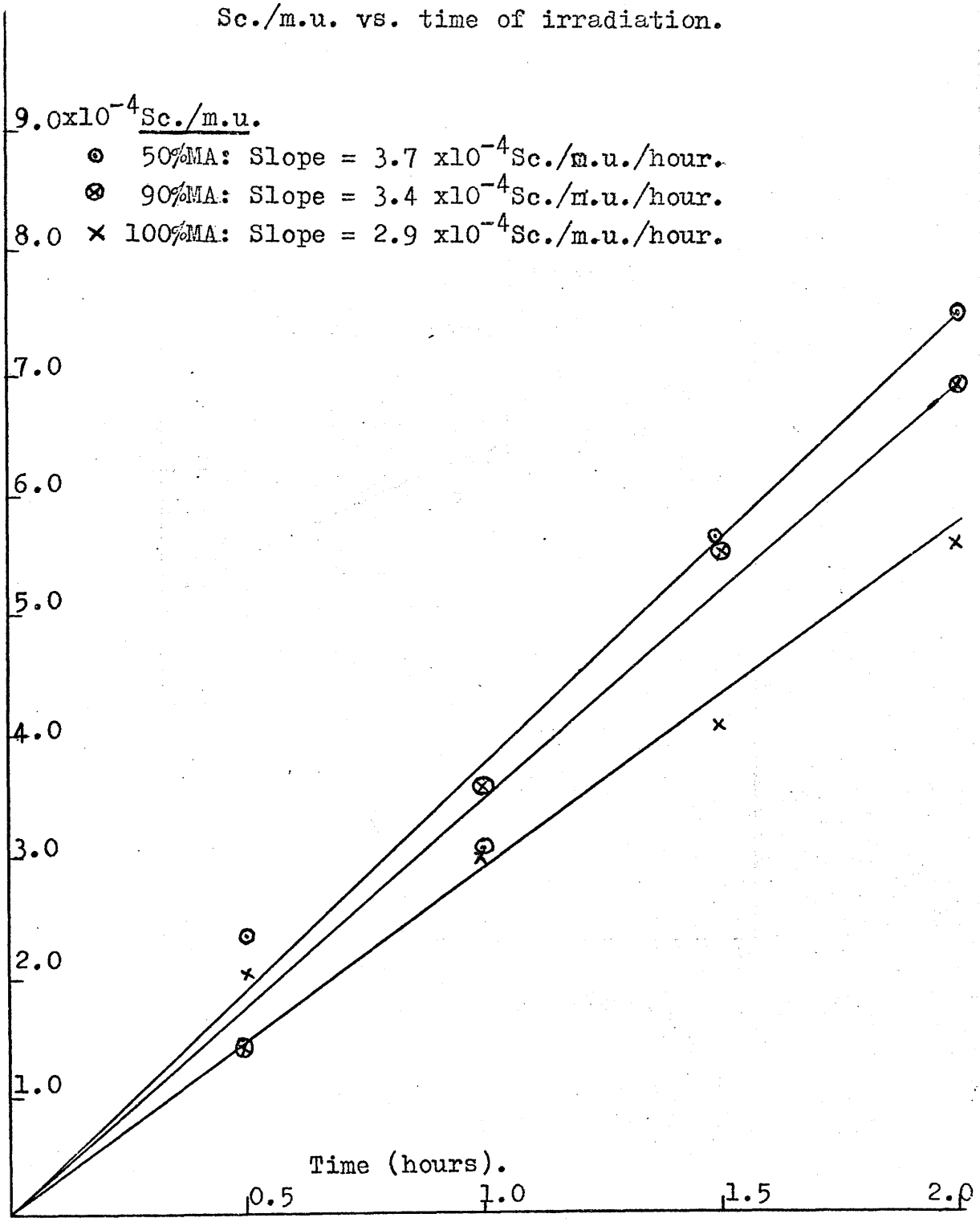


Fig. 4.x. Photo-Oxidation of Copolymers of Methyl Methacrylate and Methyl Acrylate in Methyl Acetate.

Rate of chain scission vs. Copolymer composition.

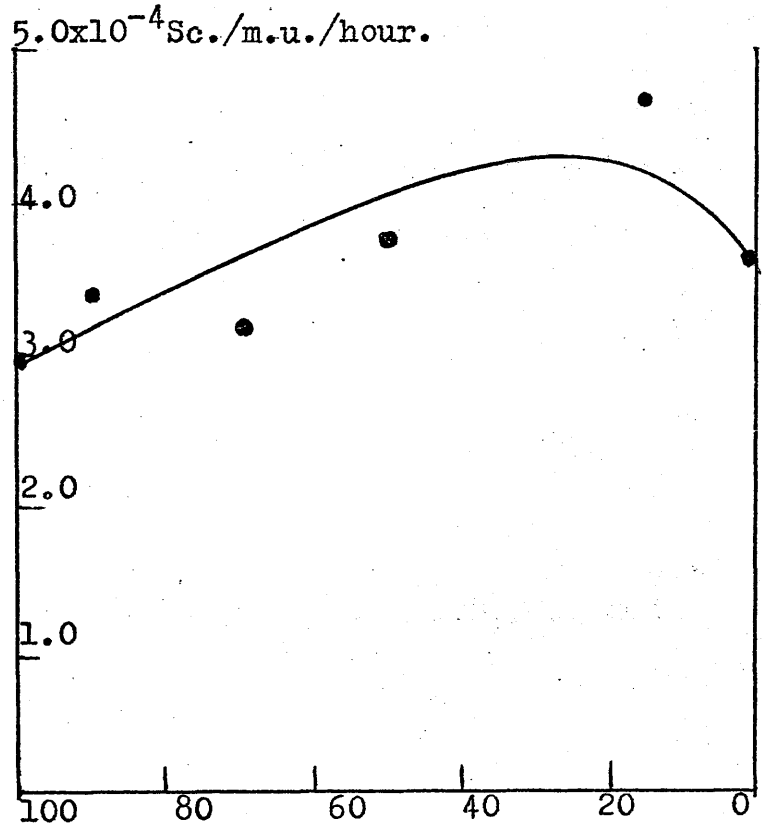


Fig. 4.xi.

Photolysis of Copolymers of Methyl Methacrylate and Methyl Acrylate under Vacuum.

Rate of chain scission vs. copolymer composition.

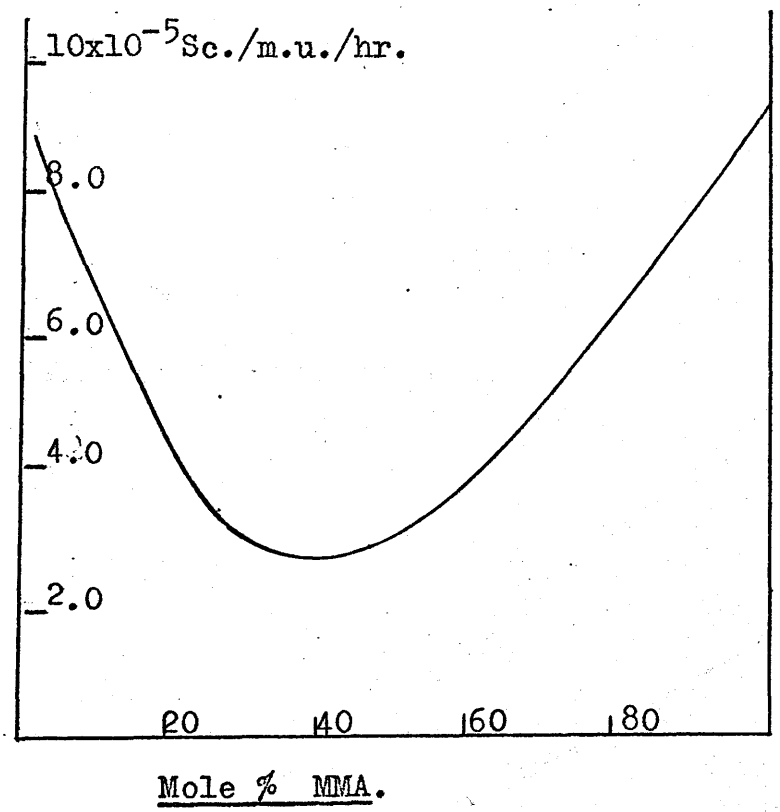


Fig. 4xii.

Irradiation of Copolymers of Methyl Methacrylate and Maleic Anhydride.

Chain scission vs. time of irradiation.

93.8%MMA. Slope=11.6x10^{-4}Sc./m.u./hr.
98.4%MMA. Slope= 8.4x10^{-4}Sc./m.u./hr.
100 % MMA. Slope= 5.4x10^{-4}Sc./m.u./hr.

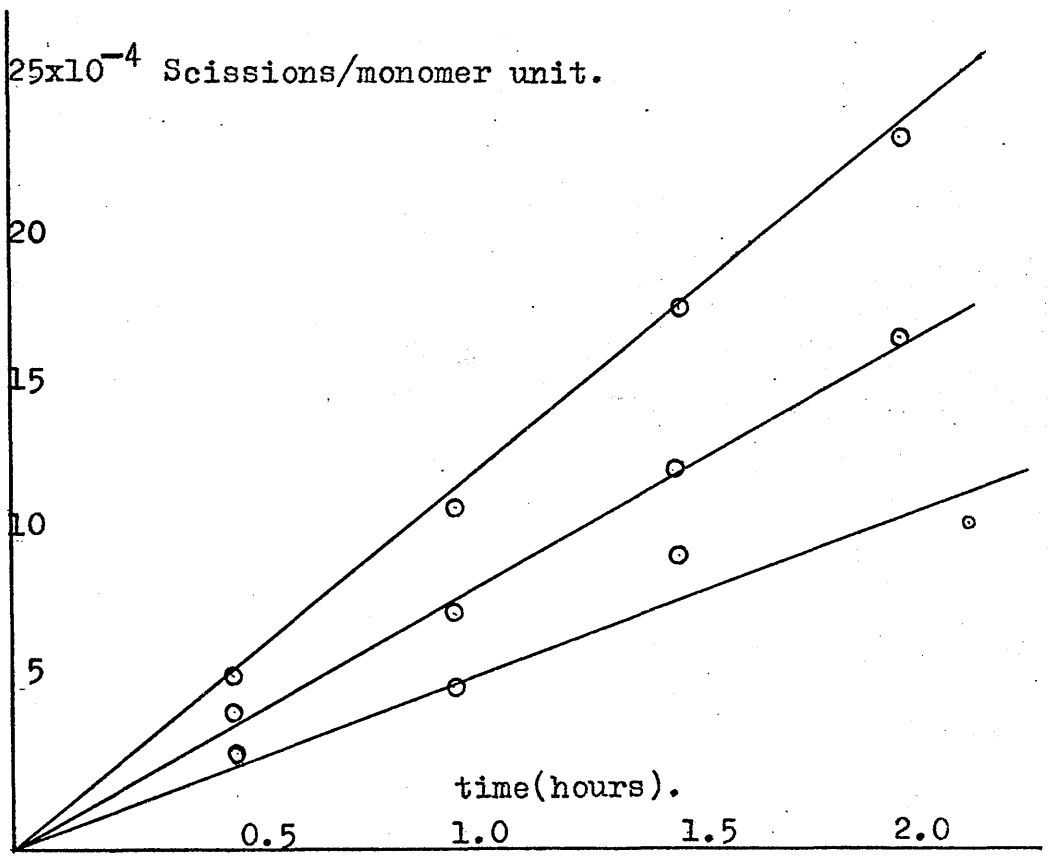


Fig.4.xiii

Irradiation of Copolymers of Methyl Methacrylate(MMA) and Maleic Anhydride.

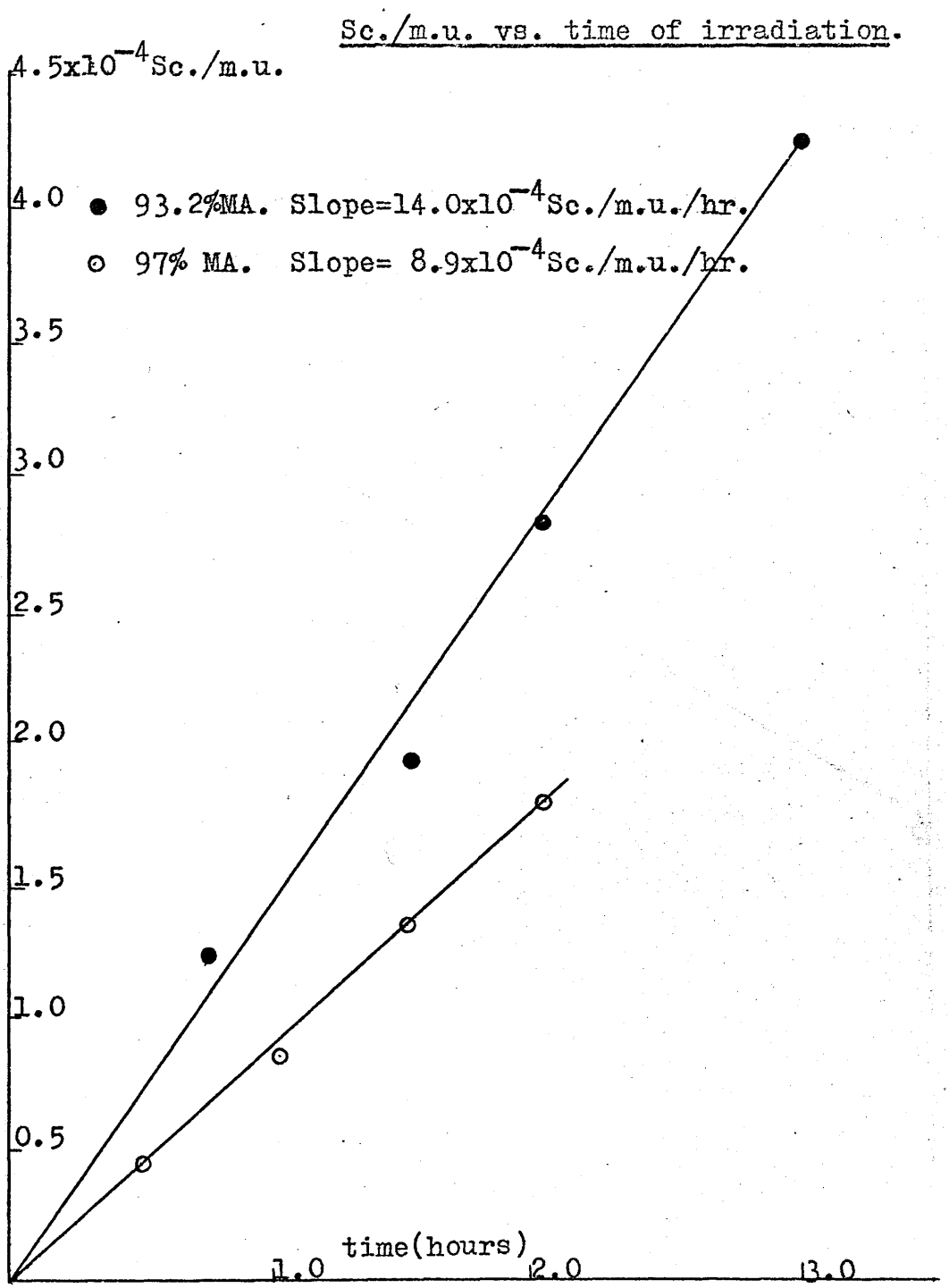


Fig. 4.xiv.

Irradiation of Copolymers of Methyl Methacrylate and Maleic Anhydride.

Rate of chain scission vs. copolymer composition.

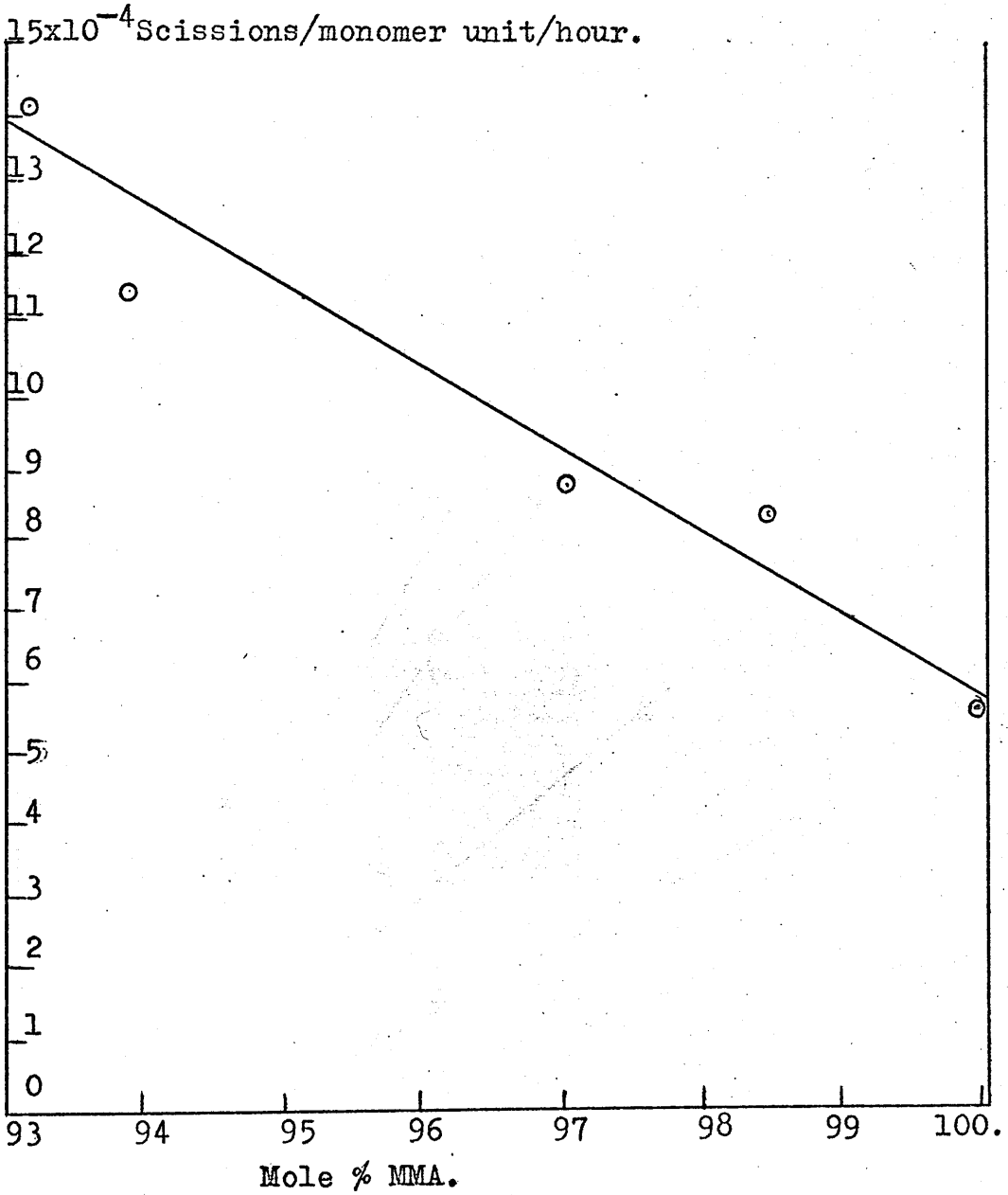
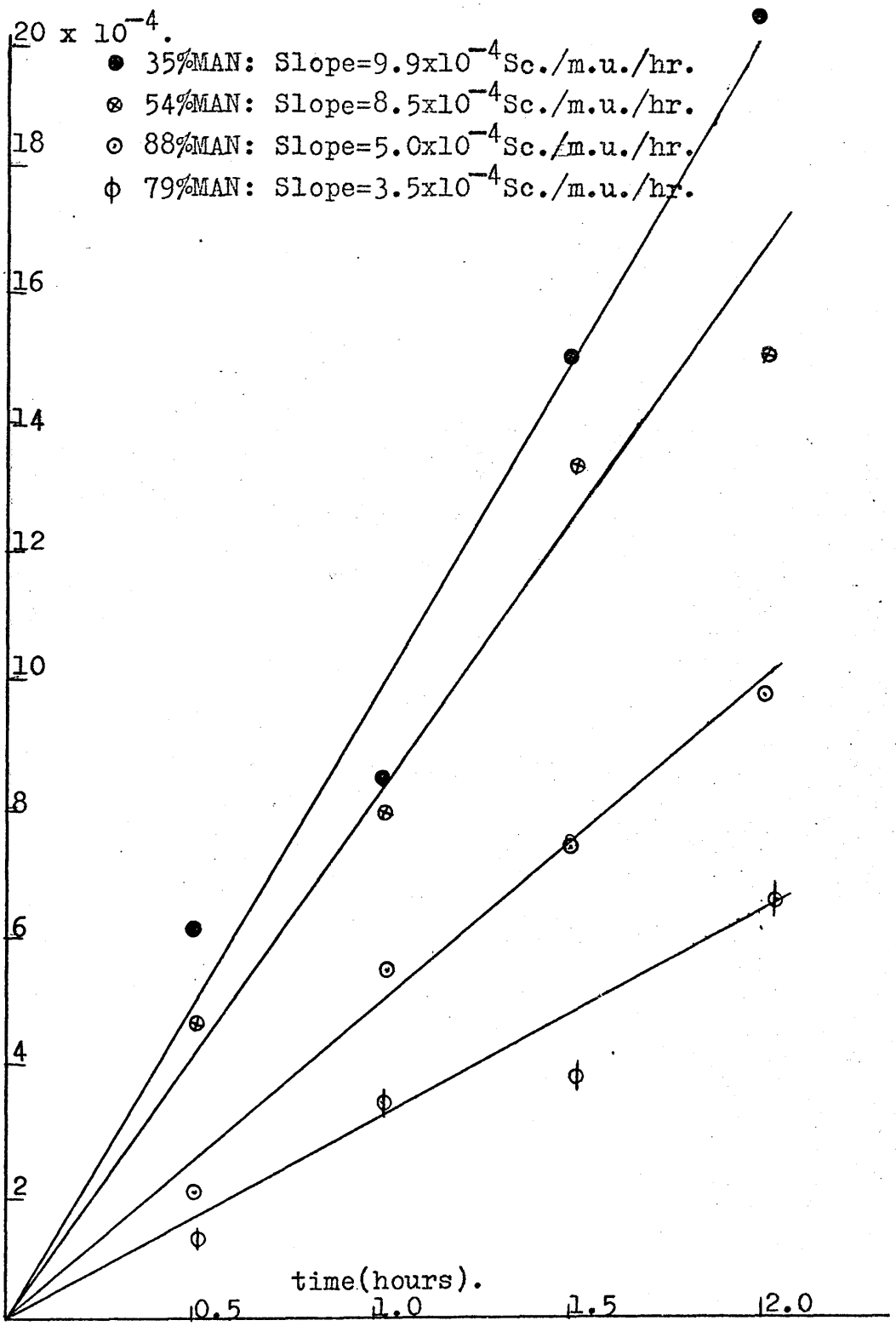


Fig.4.xv.

Irradiation of Copolymers of MMA. and MAN.

Sc./m.u. vs. time of irradiation.



Irradiation of Copolymers of MMA. and MAN.

Sc./m.u. vs. irradiation time.

Fig.4.xvi.

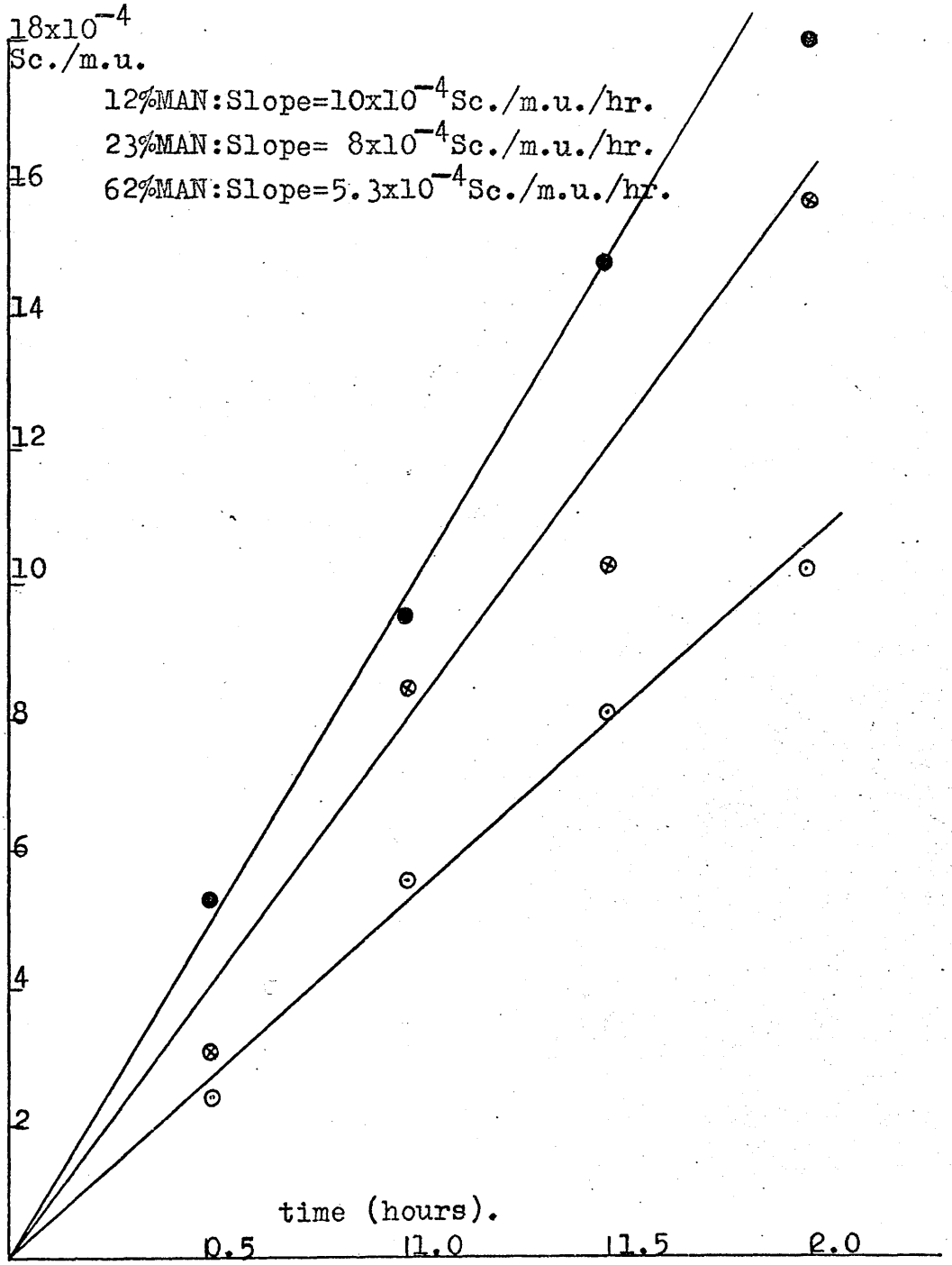


Fig 4.xvii. Irradiation of Copolymers of MMA. and MAN. Rate of chain scission vs. copolymer composition.

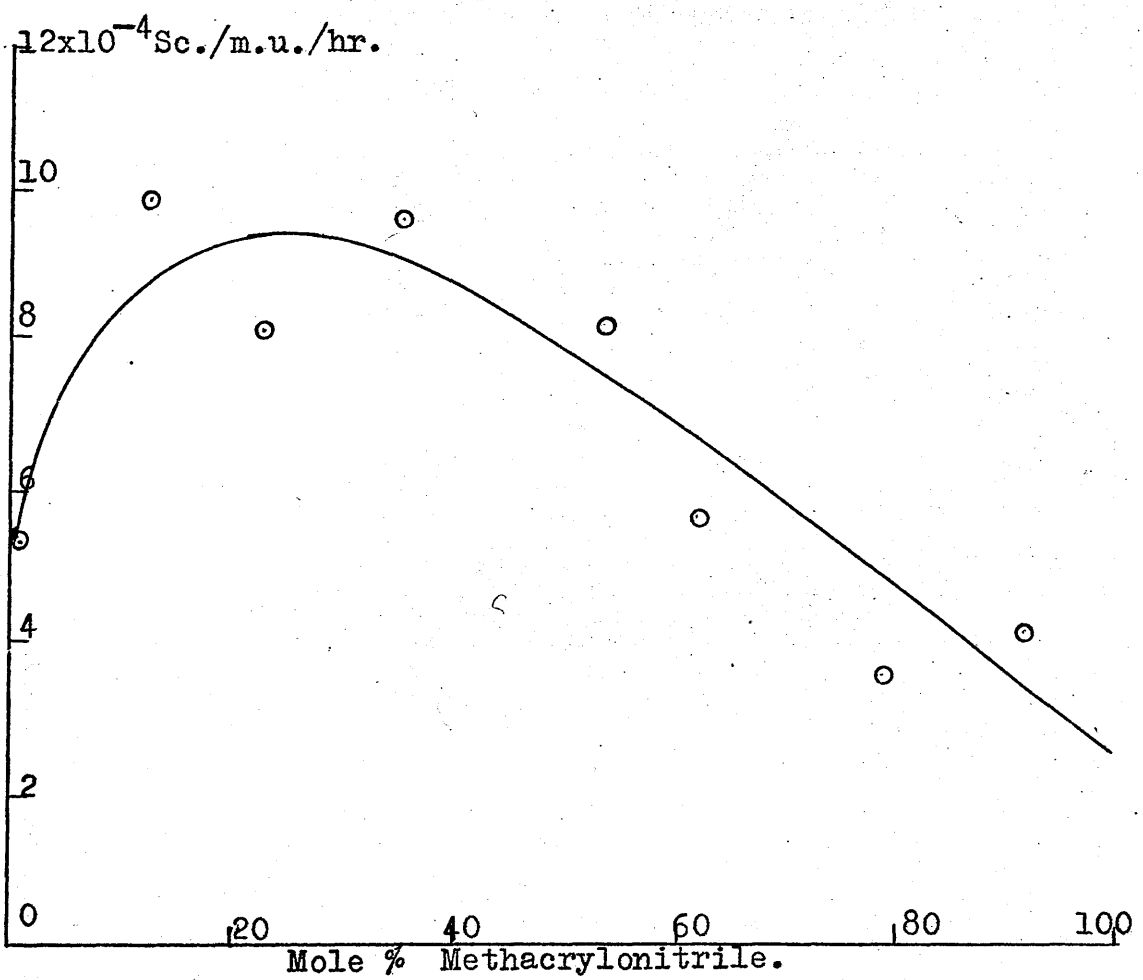


Fig.4.xviii.

Irradiation of Poly-(methyl methacrylate).

Scissions/monomer unit vs time of irradiation.

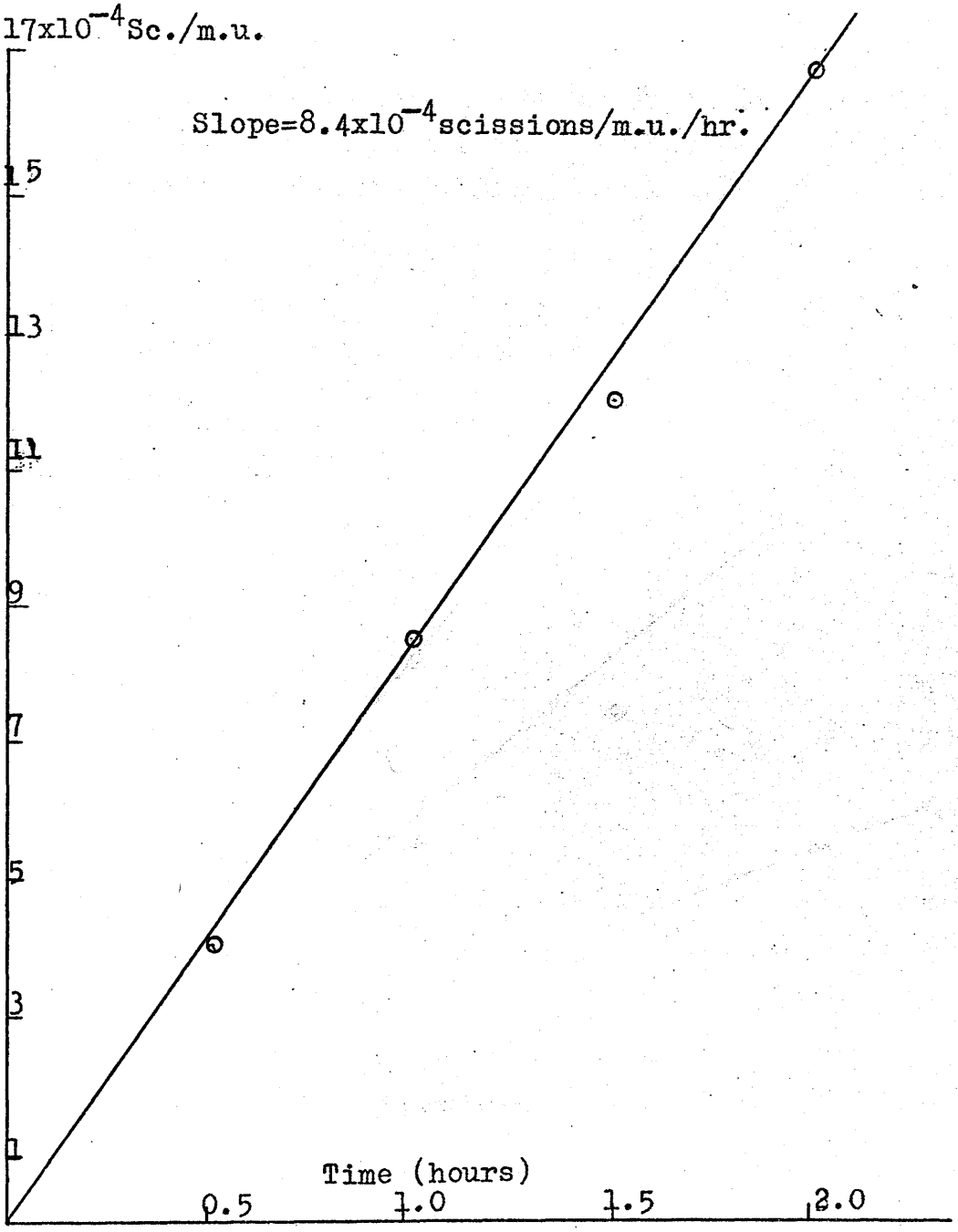


Fig. 4ixx Irradiation of Copolymers of Methyl Methacrylate and Styrene.

Scissions / monomer unit vs. time of irradiation.

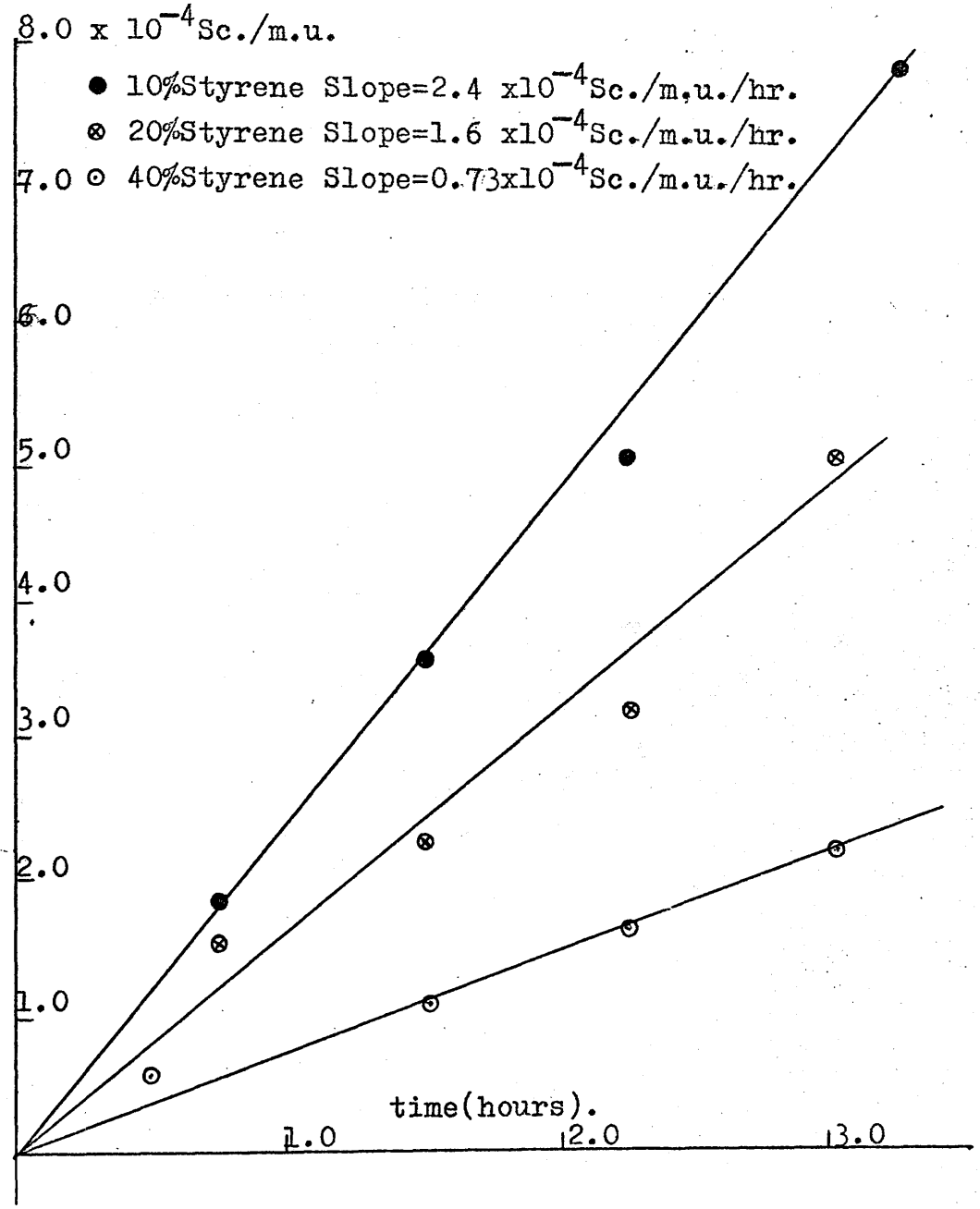


Fig. 4.xx. Irradiation of Copolymers of Methyl Methacrylate and Styrene.

Scissions/monomer unit vs. time of irradiation.

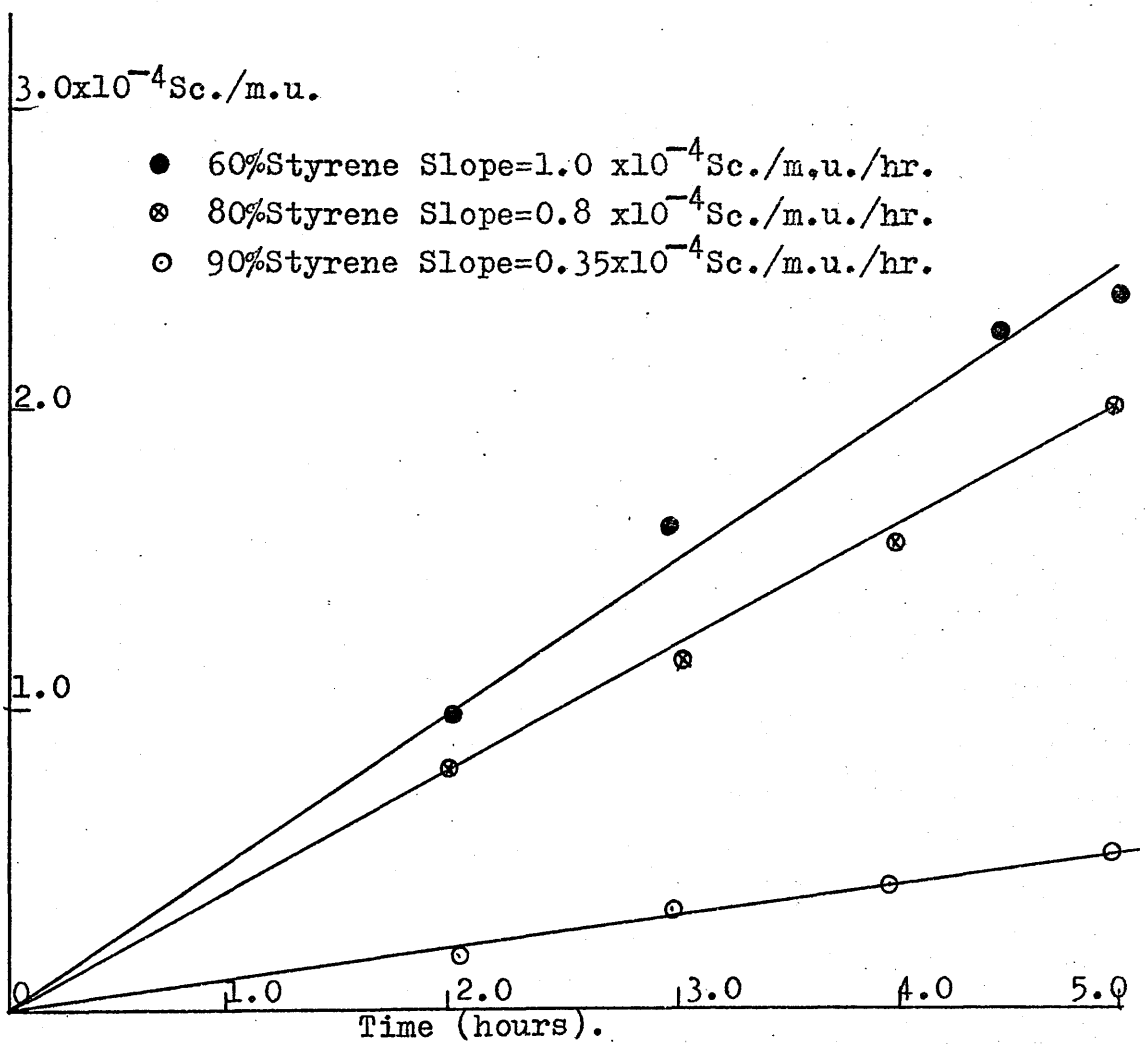
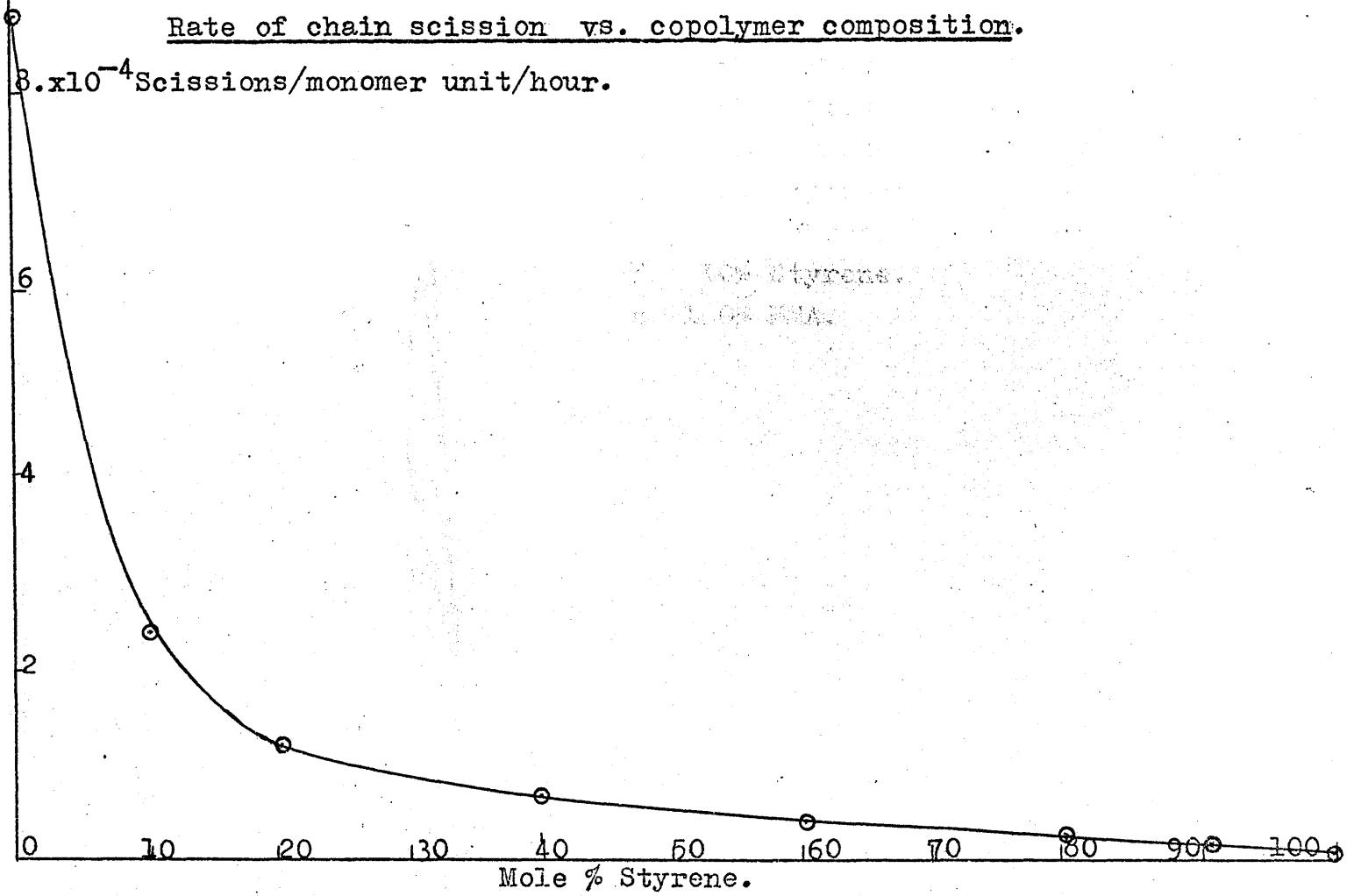


Fig.4xxi. Irradiation of Copolymers of Methyl Methacrylate and Styrene.

Rate of chain scission vs. copolymer composition.



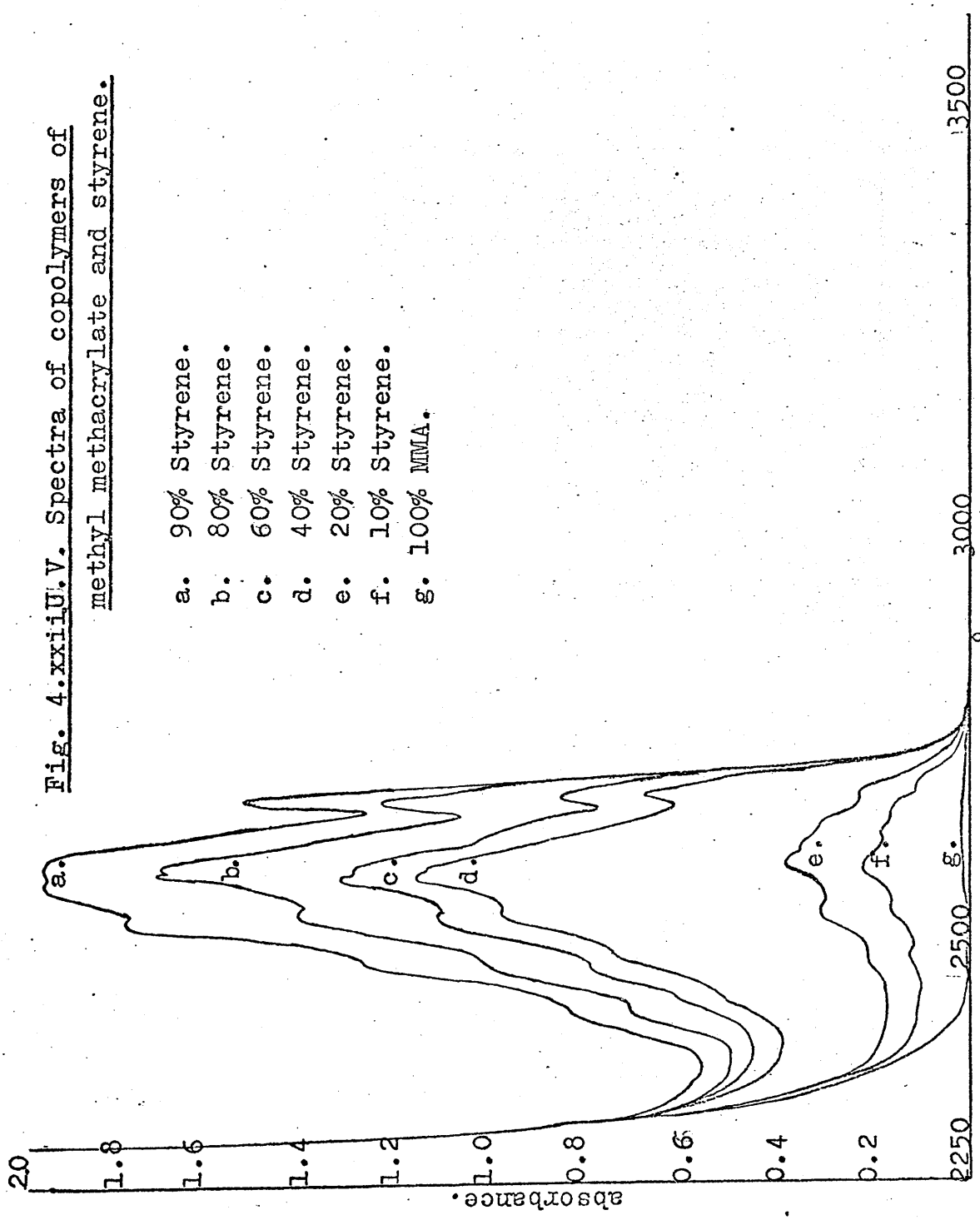
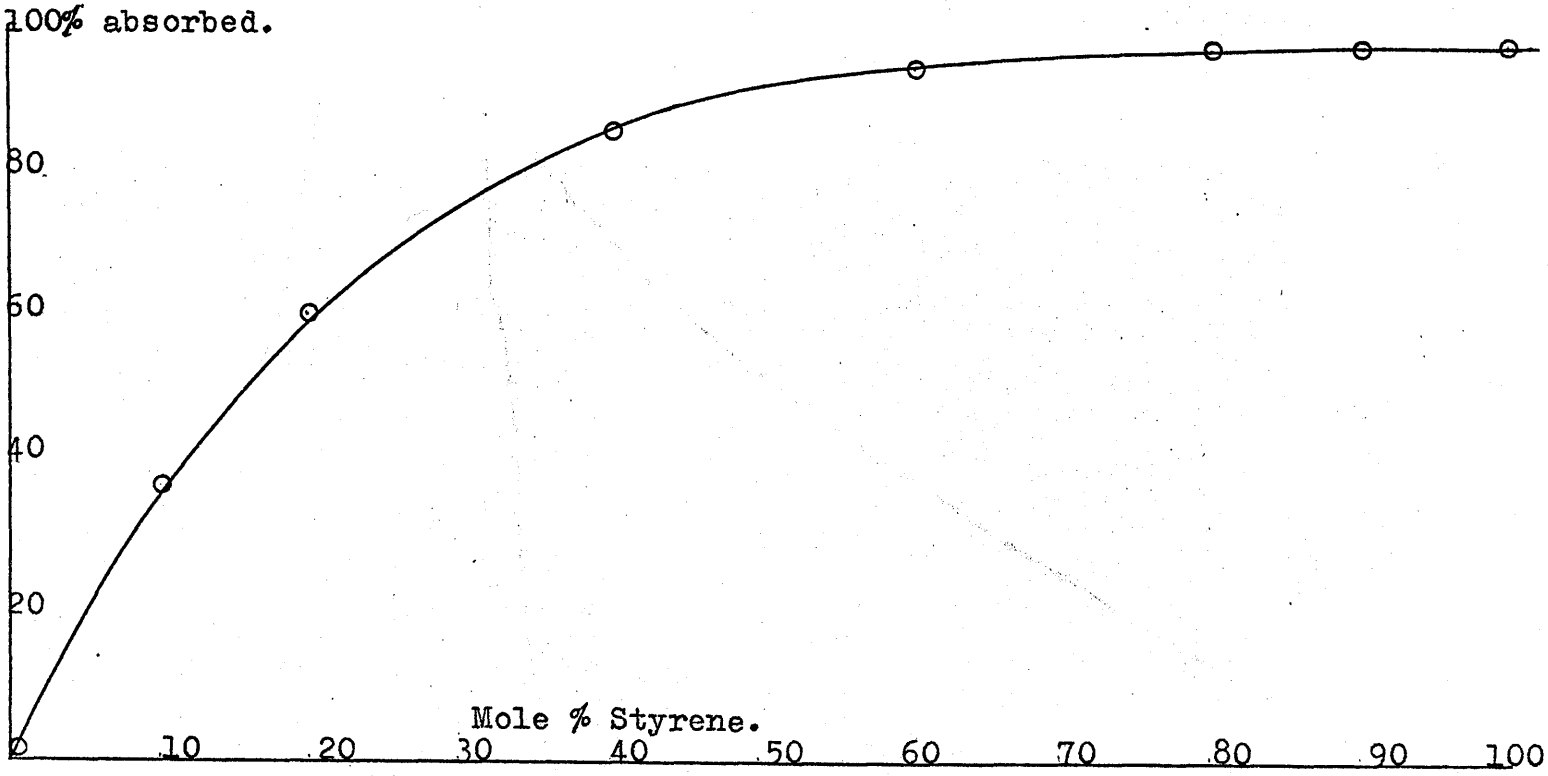


Fig. 4.xxiii. U.V. Spectra of copolymers of methyl methacrylate and styrene.

a. 90% Styrene.
b. 80% Styrene.
c. 60% Styrene.
d. 40% Styrene.
e. 20% Styrene.
f. 10% Styrene.
g. 100% MMA.

Fig.4.xxiii. % Light absorbed(2537Å) vs. Copolymer composition.

Methyl Methacrylate / Styrene Copolymers.



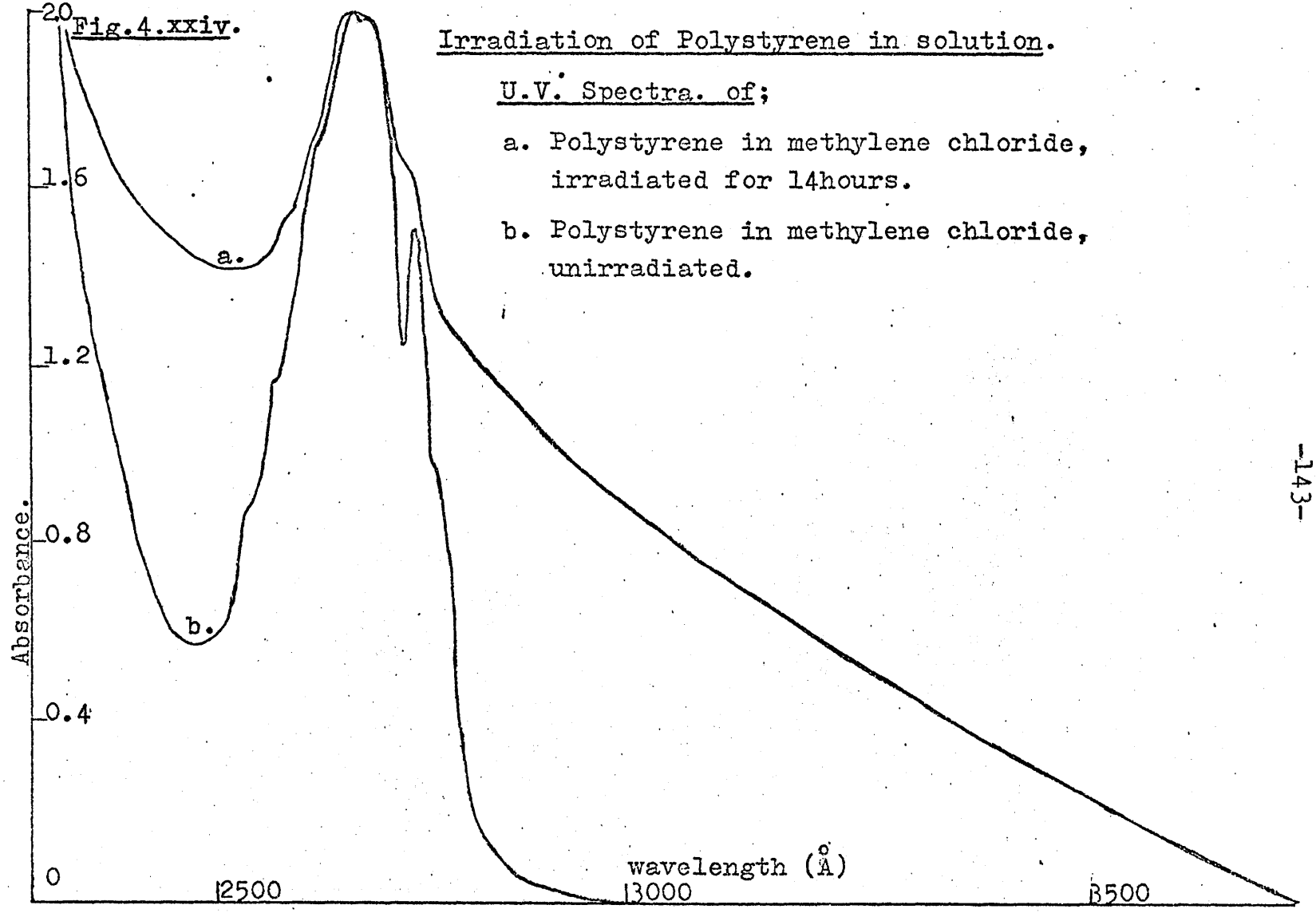


Fig.4.xxiv.
Irradiation of Polystyrene in solution.
U.V. Spectra. of;
a. Polystyrene in methylene chloride, irradiated for 14hours.
b. Polystyrene in methylene chloride, unirradiated.
Absorbance.
2.0
1.6
1.2
0.8
0.4
0
a.
b.
12500
13000
13500
wavelength (Å)

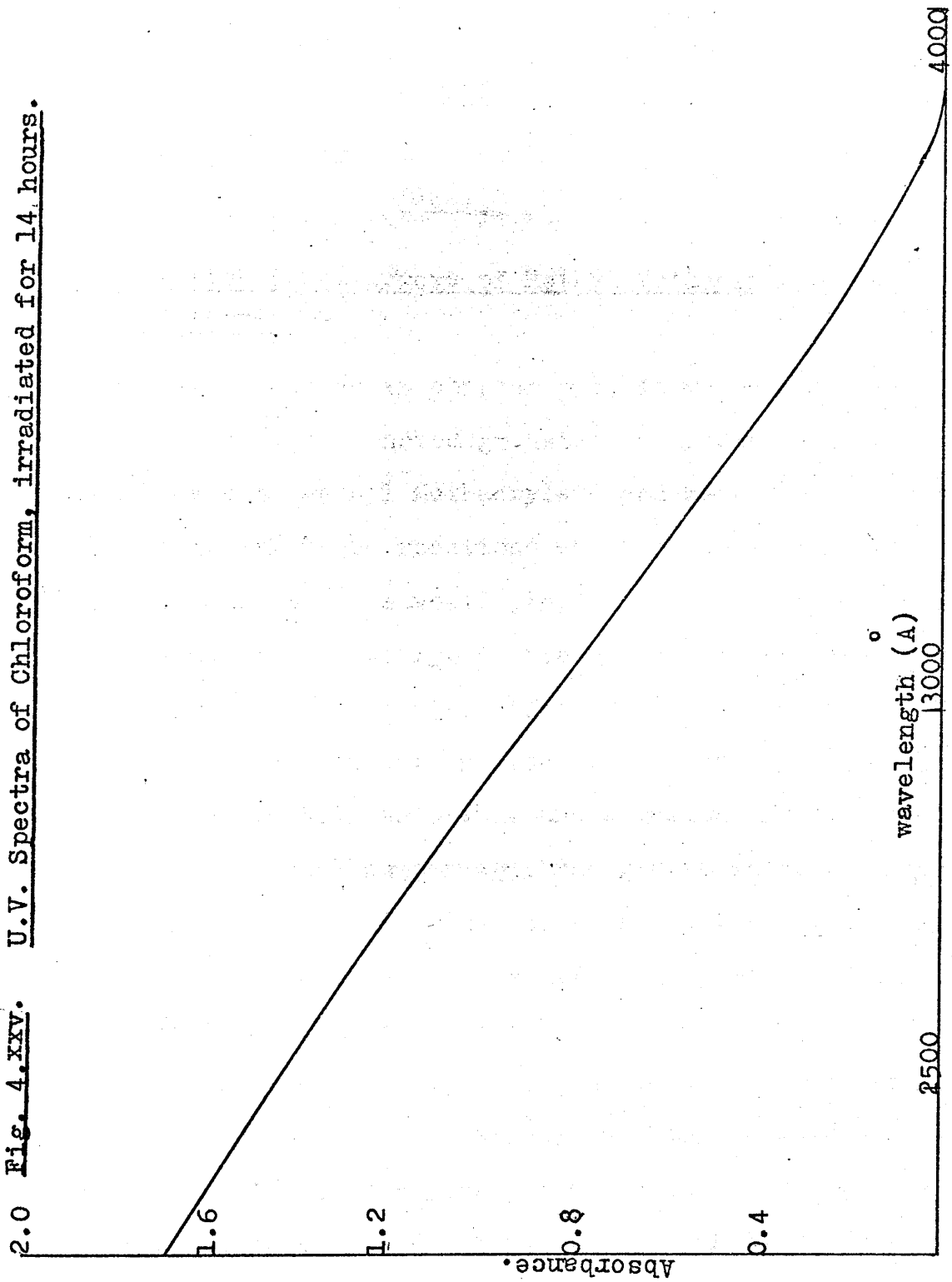


Fig. 4.xxv. U.V. Spectra of Chloroform, irradiated for 14 hours.

CHAPTER 5.

DISCUSSION.

Photolysis of Copolymers of Methyl Methacrylate and Methyl Acrylate.

As discussed in chapter one, it was considered that comparison of the photodegradation characteristics of copolymers of Methyl Methacrylate and Methyl Acrylate in solution with those reactions which occur in thin films of the same polymers would provide information which would be useful in any attempt to present a unified picture of the degradation characteristics of these polymers. In addition, photo-oxidation studies of these copolymers was undertaken in both thin film and solution and, for the purposes of ready comparison, the graphs which summarise these results are presented together in fig. 5.1. A correction has been made for the different lamp intensity used in the film photolysis.

On ultra-violet irradiation of these copolymers in the form of thin film, insolubility was observed in the residue of those copolymers in which the mole fraction of methyl acrylate exceeded 50%. Sol-gel analyses were

carried out on these copolymers and the data were analysed using the Charlesby-Pinner[75] equation,

$$s + \sqrt{s} = p_o/q_o + 1/q_o ut. \quad \text{---------- 1.}$$

where s is the soluble fraction, p_o and q_o are the rates of chain scission and crosslinking respectively, u is the number average degree of polymerisation of the starting material and t is the time of irradiation. In this work it was found that although the rate of crosslinking decreases with decreasing methyl acrylate content as expected, extrapolation suggests that it is effectively zero even in copolymers containing up to 45% methyl acrylate. It is possible then, that crosslinking is not associated with single methyl acrylate units but with sequences of two or more. For those copolymers which remain soluble, rates of chain scission were calculated from the change in molecular weight using the formula

$$n = 1/CL_t - 1/CL_o \quad \text{---------- 2.}$$

as described in chapter two.

The overall shape of the chain scission curve is perhaps unexpected. It might be reasonable to expect the rate of chain scission to decrease with decreasing MMA content at high MMA contents, but the minimum in the 40-50% MMA mole fraction region and the increase in the rate of

chain scission with increasing acrylate content until the rate in pure poly-(methyl acrylate) is of the same order as that in pure poly-(methyl methacrylate) is perhaps surprising.

The solution studies described in this thesis yielded the chain scission slope (b) in fig.5.i. It was observed that, although the rates of chain scission of poly-(methyl acrylate) and acrylate rich copolymers in film and in solution are similar, the rates of chain scission of co-polymers rich in methyl methacrylate are very much greater in solution. The possibility that crosslinking occurs in acrylate rich copolymers and thus depresses that end of the curve in fig.5.i.(b) was considered, but, as discussed in chapter three in connection with the photolysis of poly-(methyl acrylate) in solution, it may be assumed that in solution, crosslinking is not occurring to any significant extent because of the separation of polymer molecules by molecules of solvent. This was confirmed by the absence of insolubility in the residue and the observ-ation of little or no change in the rate of chain scission as a result of irradiation of polymer solutions over a wide range of polymer concentration, (1% - 10% w/v).

Since the rate of chain scission in solution, measured using equation 2, is of the same order as that observed in film photolyses using the Charlesby-Pinner equation,1, it is suggested that both of these methods for determining chain scission are reliable and that the greater rate of scission of poly-(methyl methacrylate) in solution compared with poly-(methyl acrylate) is a genuine effect which must be explained. The most significant factor in this respect is that, at ambient temperatures, the methacrylate rich copolymers are below their glass transition temperatures and those which are high in acrylate content are above theirs, the Tg.s for poly-(methyl methacrylate) and poly-(methyl acrylate) being 105°C and 6°C respectively.[76] Thus it seems reasonable to suggest that, since the methacrylate rich copolymers are relatively rigid and the polymer molecules relatively immobile, a high proportion of the primary radicals formed on bond homolysis would tend to undergo "cage effect" recombination. This would depress the inherent chain scission potential of poly-(methyl methacrylate) and copolymers of high methacrylate content. The acrylate rich copolymer molecules on the other hand are much more mobile and thus the primary radicals produced can diffuse apart much more rapidly,

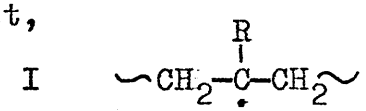
resulting in a much smaller tendency towards recombination.

In solution, this effect of Tg does not arise since the primary radicals from photolysis over the whole co-polymer composition range can diffuse apart with ease. This is reflected in a significant increase in the relative rates of chain scission of the methacrylate rich copolymers compared with that observed in film photolysis, while the rates of chain scission of acrylate rich copolymers is not significantly different in solution. To test this theory, some experiments have been carried out[73] in which the rates of photolytic scission of a high methacrylate copolymer were measured over a range of temperatures above and below the Tg of the copolymer which, measured by D.T.A., was 82°C. It was observed that the rate of chain scission increased rapidly in the region of Tg , lending support to the above argument.

Photo-oxidation of Copolymers of Methyl Methacrylate and Methyl Acrylate.

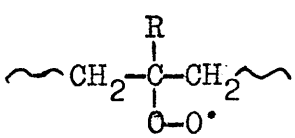
Comparison of the reactions occurring in these polymers as a result of photolysis in an atmosphere of oxygen with those occurring under vacuum conditions reveals several interesting aspects. The shape of the chain

scission curves (fig.5.i.) for photo-oxidation is considerably different to that obtained under vacuum; in both solution and film photo-oxidation, the rates of scission of poly-(methyl methacrylate) and methacrylate rich copolymers are considerably lower than those observed in vacuum and the scission reaction of poly-(methyl acrylate) and acrylate rich copolymers is accelerated in comparison with vacuum photolysis. No insoluble material was observed after photo-oxidation of the copolymer films, even in those of high acrylate content. Since in both poly-(methyl methacrylate) and poly-(methyl acrylate), chain scission results from reaction of the primary photolysis product,



I (R = H or Methyl)

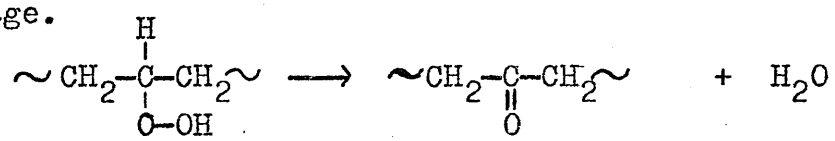
it would seem that the primary effect of the presence of oxygen must be to allow reaction of this radical with an O_2 molecule.



II

Consideration of the subsequent reactions available to this radical (II) reveals a possible explanation for some of the different characteristics found in the photo-oxidative reactions. In poly-(methyl acrylate) and high

acrylate copolymers, all or most of the groups R in radical I are H atoms and the radical has sufficient resonance stabilisation to afford combination with similar radicals resulting in the formation of crosslinks. Since radical II results from reaction with oxygen, examination of curve (c) in fig.5.i. suggests that the formation of this species causes inhibition of the crosslinking process as well as acceleration of the chain scission reaction. These observations lead to the conclusion that radical II undergoes intramolecular rearrangement, perhaps after abstraction of a H atom, to form a carbonyl group in the main chain which would result in greater susceptibility of the polymer chain to scission through Norrish Type I cleavage.



In poly-(methyl methacrylate) and methacrylate rich copolymers, all or most of the R groups are methyl groups and hence radical II is much less likely to rearrange to form carbonyl chromophores in the main chain. This results in inhibition of the chain scission reaction if some other stable product can be formed. In fig. 5.i., comparison of the curve representing the photo-oxidation of films

of the copolymers with that for photolysis under vacuum shows that acceleration of the chain scission reaction by oxygen becomes greater with decreasing acrylate content for high acrylate content polymers because of the decreasing importance of the crosslinking reaction as the relative number of sites available for crosslinking falls.

A similar effect on the chain scission reaction is found in solution photo-oxidation of these copolymers, namely inhibition of the rate in methacrylate rich polymers and acceleration in acrylate rich polymers. In this case, a less well defined maximum in the chain scission curve is observed, due probably to a combination of the acceleration and inhibition effects of the oxygen present. Fig. 5.i. shows that the relative inhibition of the chain scission reaction by oxygen in methacrylate rich copolymers in solution photolysis ($6x10^{-4}$— $3.5x10^{-4}$ scissions/monomer unit/hour) is similar to that in film photolysis, ($2x10^{-4}$—$1x10^{-4}$ scissions/monomer unit/hour). At the acrylate rich end, acceleration is much less for pure poly-(methyl acrylate) than for acrylate rich polymers, indicating that although crosslinking is inhibited, it is still a significant reaction in this polymer.

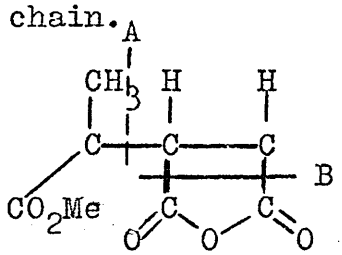
Photolysis of Copolymers of Methyl Methacrylate and Maleic Anhydride.

By far the greater proportion of the work performed on the photodegradation of polymers has been concerned with an attempt to stabilise polymers through a greater knowledge of the fundamental degradation processes which occur during photolysis. This is logical by reason of the great commercial importance of the degradative effect of sunlight on the physical properties of plastics in their practical applications. However, more recently, as a result of consideration of waste disposal and environmental pollution, some attention has been directed towards the study of possible polymer structures which could be degraded to an easily disposable form in specific environments after the useful life of the plastic article was complete. In this respect, some effort has been directed towards the preparation of photodegradable polymers.

It has been reported[77] that incorporation of a small proportion of maleic anhydride units into poly-(methyl methacrylate) causes accelerated chain scission of the polymer under thermal conditions (240°C). It was considered likely, since the anhydride group chromophore contains two carbonyl groups, that it would also have a strong

accelerating effect upon the chain scission reaction in copolymers subjected to ultra-violet radiation.

The results of this phase of the work are summarised in fig. 4.xiv and the general conclusion is that incorporation of even a small percentage of maleic anhydride as comonomer into poly-(methyl methacrylate) accelerates its rate of photodegradation by chain scission. As discussed earlier, low temperature photolysis of poly(methyl methacrylate) homopolymer films results in random cleavage of the ester side groups, followed by chain scission of the resulting polymer radical. The acceleration of the chain scission reaction by maleic anhydride units in these copolymers would appear to be a result of initial cleavage of the labile C—C bond (A) next to the anhydride unit in the polymer chain.



Cleavage of the bonds (B) would result in the destruction of the anhydride group and this would be revealed by the disappearance of the anhydride absorption characteristics in the infra-red spectrum of the irradiated polymer.

No significant change in the infra-red spectra of the irradiated polymers was in fact observed. Thermal studies (240°C) on this copolymer system[77] also suggested that the acceleration of the chain scission reaction was due to preferential cleavage of the C—C bond next to the anhydride group, since, even after degradation for four hours at 240°C, the anhydride group absorption was still very strong. Earlier discussion of the photolysis of poly-(methyl methacrylate) in solution at ambient temperatures indicated that no depropagation occurred, since, within experimental error, the polymer was 100% recoverable by weight after irradiation. However, the results of both thermal[77] degradation and photothermal[78] degradation at 150°C suggest that although the anhydride groups initiate chain scission, they strongly block the depropagation reactions. In drawing the curve of rate of chain scission versus co-polymer composition (fig.4.xiv) it has been assumed that a linear relationship exists over the rather restricted range of copolymer composition studied. Over a wider range, this may not be the case. In addition, over the time interval of the irradiations, up to four hours, the rates of chain scission versus time of irradiation were found to be linear, but for low anhydride content copolymers, this would not be true over longer periods of irradiation

since after scission at an anhydride group in a chain which is effectively poly-(methyl methacrylate) with an anhydride end group, pure poly-(methyl methacrylate) chains would come into existence, causing the rate of chain scission of the remaining polymer to approach that of pure poly-(methyl methacrylate). Drawing a comparison with copolymers of methyl methacrylate and methyl acrylate of high methacrylate content, it is not surprising that crosslinking was never detected after subjecting these copolymers to ultra-violet radiation. Crosslinking is unlikely since the number of potential crosslinking sites is very small and the polymer molecules are separated by molecules of solvent.

Photolysis of Copolymers of Methyl Methacrylate and Methacrylonitrile and Styrene.

In the study of the photolysis of copolymers of methyl methacrylate and methyl acrylate, several interesting trends in the degradation characteristics across the copolymer composition range were indicated. Methyl acrylate is structurally very similar to methyl methacrylate, having an identical chromophore, the ester group. Because of this, it was thought that further valuable information might be obtained by irradiating methyl methacrylate copolymerised with monomers having different chromophores. The comonomers chosen were methacrylonitrile and styrene. The former is of interest since it has a similar structure to methyl methacrylate but with the C≡N chromophore which does not absorb appreciably at 2537Å. The latter, styrene, contains a strongly absorbing aromatic nucleus.

Photolysis of Copolymers of Methacrylonitrile.

The chain scission results of the photolysis of copolymers of methyl methacrylate and methacrylonitrile are illustrated in fig.4xvii, the detailed shape of which is difficult to explain. As mentioned in chapter three, the insolubility of these copolymers in toluene necessitated the use of cyclohexanone as solvent for osmotic molecular weight determinations. This solvent has a strong affinity

for water, readily absorbing it from the atmosphere. Although freshly distilled solvent was used throughout, it is possible that this deliquescent tendency contributed to less reliable osmotic results than when toluene was used for the other copolymer systems. Hence, any explanation of the results of this work must be formulated with this in mind. However, from fig.4xvii, it would seem that incorporation of a few methacrylonitrile units into poly-(methyl methacrylate) has a destabilising effect on the polymer, although further increase in the methacrylonitrile content yields smaller rates of chain scission until methacrylonitrile rich copolymers were observed to undergo chain scission at much the same rate as poly-(methyl methacrylate). No literature information about the photodegradation of methacrylonitrile copolymers is available. However, Grassie and Farish[79] studied the action of 2537Å radiation at 160°C on copolymers of methyl methacrylate and acrylonitrile in the composition range 0.25%—10% mole% acrylonitrile. It was found that the rate of the chain scission reaction increased with increasing acrylonitrile content. This would seem to agree with the results of this work for methacrylate rich copolymers. It is worth noting here that in solution work, it is highly

impractical to detect and characterise small molecule fragments arising as products of the reactions occurring since they are in such small concentration relative to the concentration of solvent. As a consequence, it is difficult to formulate a mechanistic explanation for the destabilisation influence of methacrylonitrile.

Photolysis of Copolymers of Styrene.

The aromatic ring in polystyrene absorbs 2537Å radiation strongly and it was this characteristic which stimulated an investigation of the photolysis of copolymers of methyl methacrylate and styrene. It seemed reasonable to expect that copolymerisation of styrene with methyl methacrylate would lead to either of two possibilities when the polymer was subjected to photolysis by 2537Å radiation. Firstly, the enhanced quantity of absorbed radiation energy could be transferred along the polymer molecule as mentioned in chapter one, causing cleavage of the more labile bonds in the molecule. If this were the case, incorporation of styrene into poly-(methyl methacrylate) would be expected to result in an increase in the rate of chain scission of methacrylate rich polymers with increasing styrene content. On the other hand, if

the absorbed energy is not transferred along the polymer but is dissipated as heat or by phosphorescence, fluorescence etc, the strongly absorbing site could as an optical filter, the overall effect being, as in polystyrene itself, one of protection of the polymer by preferential absorption at stable sites on the polymer chain. The rates of chain scission observed on photolysis of these copolymers are illustrated in fig.4.xxi. It can be seen that the rate of chain scission rapidly falls from that of pure poly-(methyl methacrylate) with increasing styrene content up to around 20 mole %, and then gradually tails off to almost zero for 100% polystyrene. It seems that since the sharp decrease in the rate of chain scission is accompanied by a sharp increase in absorption of 2537Å radiation by the copolymer, the styrene aromatic rings are having the effect of stabilising the copolymer against radiation by means of preferential absorption at the stable aromatic rings. The absorbed energy must be dissipated from the aromatic nuclei by methods other than by energy transfer along the polymer chain. As with the photolysis of poly-(methyl acrylate) in solution, no insolubility of polystyrene or styrene rich polymers was detected in the

residue of the irradiated polymers.

Chain scission of copolymers of methyl methacrylate and styrene in film form[80] during photolysis is difficult to assess since, because of the strong absorption of 2537Å radiation by styrene, reaction only occurs at the surface, even for thin films, and insolubility is encountered as in pure polystyrene. Since this work was carried out in solution with constant stirring, these difficulties were overcome and it has been shown that incorporation of a small amount of styrene as comonomer has a significant stabilising effect upon poly-(methyl methacrylate).

Coloration of Polystyrene.

The occurrence of yellowing in aged polystyrene has been well documented and has usually been associated with oxidation of the polymer. Fox and coworkers[33] noted a "general featureless" increase in absorbance at wavelengths above 2500Å in films which had been irradiated under vacuum but much smaller than that after photolysis in air. Grassie and Weir[81] also noted an increase in absorbance at these wavelengths and suggested that oxygen was not a prerequisite for the yellowing reaction, the yellowing being attributed to conjugated unsaturation in the polymer backbone, a peak at 825cm^{-1} in the infra-red

spectrum being allocated to main chain unsaturation. During solution photolysis of the copolymers of styrene and methyl methacrylate, it was noted that long irradiations (12 hours) of polystyrene and styrene rich copolymers in methylene chloride resulted in yellowing of the solution and this observation prompted an examination of the coloration reaction in these copolymers. However, when this coloration was observed on long irradiations of all of the copolymers, even methacrylate rich copolymers, some doubt was cast as to the nature of the coloration. Further irradiations of polystyrene in the solvents--methylene chloride, chloroform, chloroethane, cyclohexane and methyl acetate resulted in similar coloration in the first three solvents and none in the others. Irradiation of these solvents in the pure state yielded similar results, coloration being observed in the irradiated chlorinated hydrocarbons and none in methyl acetate and cyclohexane. It was concluded that the coloration in this case was due to photolysis of the chlorinated hydrocarbons and not of the polystyrene. In the light of this information, the coloration of polystyrene films in vacuum was considered since those investigated previously[81] had been cast from

a chlorinated hydrocarbon, chloroform, the removal of residual chloroform being monitored by the disappearance of the $CHCl_3$ peak at 1218cm^{-1} in the infra-red spectrum. The first drying method, described in 2.4.b, used in this work also yielded polystyrene films which did not show any appreciable peak at 1218cm^{-1} in the infra-red spectrum. However, the films dried by this method were subjected to Thermal Volatilisation Analysis as described in chapter 4 and showed a small solvent volatilisation at 116°C, close to the M.Pt. of polystyrene. These films displayed appreciable coloration when irradiated in vacuum, the ultra-violet spectra of the irradiated film being similar to that of the irradiated chlorinated hydrocarbon solvents as shown in figs.4. xxiv and xxv. Films which were dried by the more stringent method described in 2.4.c, did not show coloration on irradiation for similar periods of time. These observations suggest that polystyrene itself does not undergo a coloration reaction during vacuum photolysis and that the coloration observed in aged polystyrene indeed must be the result of an oxidation reaction.

Suggestions for Future Work.

A useful extension of the photolysis of polymeric materials in solution would be the photolysis of polymers in solutions containing hydrolytic agents like water, acid and alkali. In particular, the study of condensation polymers which are known to be susceptible to hydrolysis- polyesters, for example poly-(ethylene terephthalate) and polyamide nylons. This could yield useful information concerning the interaction of these two degradative influences on polymeric materials.

With reference to photodegradable polymers, discussed in chapter 5, the results of the photolysis of maleic anhydride copolymers have shown that incorporation of a small quantity of this monomer can have some interesting effects. It would be of interest to study the photolysis of some other monomers copolymerised with a little maleic anhydride in an attempt to generalise the effects of the anhydride group on the photostability of polymers.

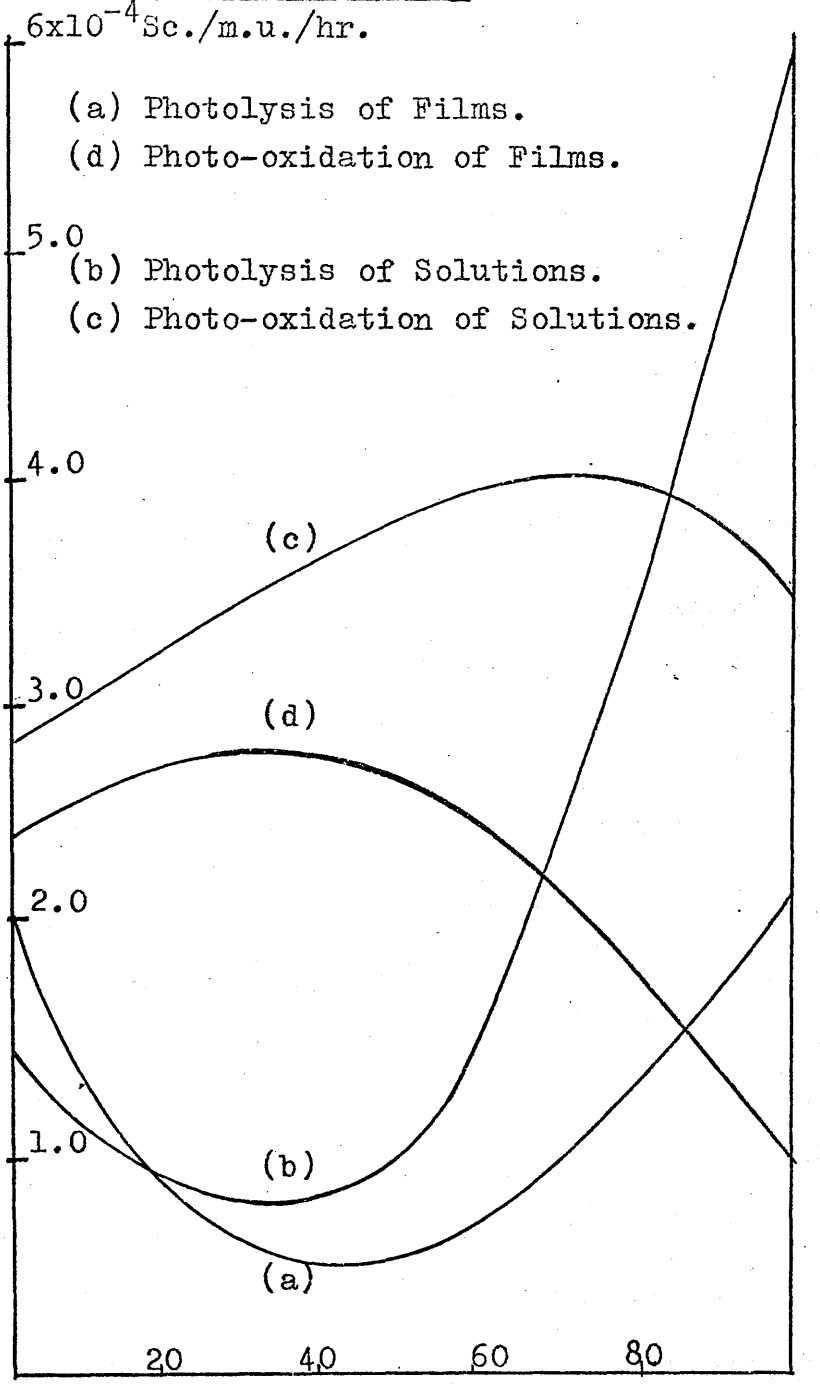
Also, since poly-(methyl isopropenyl ketone) has been reported[14] to be very unstable to ultra-violet radiation, it would be interesting to use small quantities of

methyl isopropenyl ketone as comonomer with methyl methacrylate to ciscover whether it would also have a destabilising effect upon poly-(methyl methacrylate) with regard to photo-induced chain scission.

In view of the encouraging results of the application of infra-red spectroscopy to determine the composition of copolymers of methyl methacrylate and maleic anhydride, it would be useful to apply this technique to a larger range of copolymer composition. Work has already begun[78] along these lines in conjunction with a detailed study of the photo and photothermal degradation of this copolymer system.

Since the physical properties of polymers like poly-(vinyl chloride), polyethylene and polypropylene deteriorate very rapidly when exposed to sunlight, the possibility of incorporating a little styrene as comonomer in these materials to give the effect of an optical filter, as observed with methyl methacrylate copolymers, might be studied.

Fig. 5.i. Photolysis of Copolymers of Methyl Methacrylate and Methyl Acrylate.



REFERENCES

1. C.M. Masson, V. Boekelheide, W.A. Noyes,Jr., "Photochemical Reactions" in "Technique in Organic Chemistry" Vol.2, A. Weissberger,ed., Interscience, New York 1956 (2nd. Ed.).

2. J.G. Calvert and J.N. Pitts,Jr., "Photochemistry" John Wiley and Sons, New York, 1967.

3. P.A. Leighton and G.S. Forbes, J.Amer. Chem. Soc., 52 3139 (1930).

4. G.S. Forbes and L.J. Heidt, J.Amer. Chem. Soc., 56 2363 (1934).

5. C.G. Hatchard and C.A. Parker, Proc. Roy. Soc., A235, 518 (1956).

6. C.A. Parker, Proc. Roy. Soc., A220 104 (1953).

7. H.H. Jellinek and I.J. Bastien, Can. J. Chem., 39 2056 (1961).

8. L.G. Isaacs in R.B. Fox, "Photodegradation of High Polymers", in "Progress in Polymer Science", Vol.1, A.D. Jenkins, ed., Pergamon Press, London,(1967)

9. R.P. Wayne, Photochemistry Butterworths.

10. R.G.W. Norrish and C.H. Bamford, Nature, 140 195 (1937).

11. C. David, W. Demartreau and G. Geuskens, Polymer, 8 497 (1967).

12. J.E. Guillet and R.G.W. Norrish, Proc. Roy. Soc., A233 153 (1956).

13. K.F. Wissburn, J.Amer. Chem. Soc., 81 58 (1959).

14. A.R. Shultz, J. Polym. Sci., 47 267 (1960).

15. R.B. Fox, "Photodegradation of High Polymers" in "Progress in Polymer Science", Vol.1, A.D. Jenkins,ed., Pergamon Press, London,(1967).

16. A. Charlesby,G.S. Grace and F.B. Pilkington, Proc. Roy. Soc., A268 205 (1962).

17. R.B. Fox and T.R. Price, J. Polym. Sci., A3 2303 (1965).

18. R.B. Fox and T.R. Price, Organic Coatings and Plastics Chem. Div., Amer. Chem. Soc. Preprints 25 (2) 138 (1965).

19. R.B. Fox, L.G. Isaacs and S. Stokes, J. Polym. Sci., A1 1079 (1963).

20. S. Stokes and R.B. Fox, J. Polym. Sci., 56 507 (1962).

21. S.L. Madorsky, S. Straus, D. Thompson and L.Williamson, J. Res. Nat. Bur. Stand. 42 499 (1949).

22. N. Grassie, Chemistry of High Polymer Degradation Processes Butterworths, London, (1956).

23. J.R. M^{c}Callum, Makromol Chemie, 83 129 (1965).

24. P.R.E.J. Cowley and H.W. Melville, Proc. Roy. Soc., A210 461 (1952) and A211 320 (1952).

25. N. Grassie and H.W. Melville, Proc. Roy. Soc., A199 1,14, 24,39(1949).

26. J.R. M^{c}Callum, Eur. Polym. J., 2 413 (1966).

27. K.F. Wissburn, J. Amer. Chem. Soc., 81 58 (1959).

28. F.S. Dainton and K.J. Ivin, Nature, 162 705 (1948).

29. F.S. Dainton and K.J. Ivin, Trans. Faraday Soc., 46 331,374,382 (1950).

30. F.S. Dainton and K.J. Ivin, Proc. Roy. Soc., A212 96 207 (1952).

31. F.S. Dainton and K.J. Ivin, Disc.Faraday Soc., 14 199 (1953).

32. F.W. Billmeyer, Textbook of Polymer Science, Interscience New York (1962).

33. R.B. Fox, L.G. Isaacs, R.E. Saalfeld and M.V. M^{c}Dowell, U.S. Naval Res.Lab. Rept. No.6284 (1965).

34. N. Grassie and N.A. Weir, J. Appl. Polym. Sci., 9 975 (1965).

35. R.B. Fox, L.G. Isaacs, S. Stokes and R.E. Kagarise J. Polymer Sci., A2 2085 (1964).

36. R. Simha, J. Polym. Sci., 9 465 (1952).

37. P.A. Small in P.R.E.J. Cowley and H.W. Melville, Proc. Roy. Soc., A210 461 (1952).

38. M.I. Frolova and A.V. Riabov, Vysokomol. Soedin, 3 877 (1961) in R.B. Fox, "Photodegradation of High Polymers", in "Progress in Polymer Science" Vol.1, A.D. Jenkins (ed.) Pergamon Press, London, (1967).

39. A.R. Shultz, J. Phys. Chem., 65 967 (1961).

40. A.R. Shultz, P.I. Roth and G.B. Rathman, J. Polym. Sci., 22 495 (1956).

41. G. Oster, G.K. Oster and H. Moroson, J. Polym. Sci., 34 671 (1959).

42. H. Monig, Naturwiss, 45 12 (1958).

43. A. Charlesby and D.K. Thomas, Proc. Roy. Soc., A269 104 (1962).

44. A. Charlesby and N. Moore, Int. J. Appl. Radiation and Isotopes 15 703 (1964).

45. L.D. Maxim and C.H. Kuist, Polymer Preprints, 4 352 (1963).

46. N.S. Kardash and V.A. Krongauz, Vysokomol Soedin Ser. B., 10 271 (1968); CA 69 10912n (1968).

47. R.B. Fox and T.R. Price, Polymer Preprints 5 390 (1964).

48. R.B. Fox and T.R. Price, J. Appl. Polym. Sci., 11 2303 (1967).

49. H. Monig and H. Kriegel, Proc. 3rd. Int. Congress on Photo-Biology, Copenhagen (1960).

50. H. Monig and H. Kriegel, Z. Naturforsch., 15b 333 (1960).

51. H. Monig and H. Kriegel, Biophysik, 2 22 (1964).

52. H.H.G. Jellinek and I.C. Wang, Kolloid-Z.und Z. Polymere, 202 1 (1965).

53. J.P. Allison, J. Polym. Sci., A1 4 1209 (1966).

54. N. Grassie, B.J.D. Torrance and J.B. Colford, J. Polym. Sci., A1 7 1425 (1969).

55. N. Grassie and B.J.D. Torrance, J. Polym. Sci., A1 6 3033 (1969).

56. A. Scotney, Private Communication.

57. See reference no. 15.

58. R. Simha and H. Bransen. J. Chem. Phys. 12 253 (1944).

59. T. Alfrey Jr. and G. Goldfinger, J. Chem. Phys. 12 205 (1944).

60. F.T. Wall J. Amer. Chem. Soc., 66 2050 (1944).

61. F. Mayo and F.M. Lewis, J. Amer. Chem. Soc., 66 1594 (1944).

62. N. Grassie, B.J.D. Torrance, J.D. Fortune and J.D. Gemmill, Polymer, 6 653 (1965).

63. F.M. Lewis, C. Walling, W. Cummings, E.R. Briggs and F.R. Mayo, J. Amer. Chem. Soc., 70 1519 (1948).

64. P.C. Blackley and H.W. Melville, Mak. Chemie, 18 19 (1956).

65. F.M. Lewis, C.Walling, W. Cummings, E.R. Briggs and K. Wenisch, J. Amer. Chem. Soc., 70 1527 (1948).

66. H.T. Hookway, "Techniques of Polymer Characterisation" Ed. P.W. Allen, Butterworths (1959).

67. Mechrolab Model 501 High Speed Membrane Osmometer Instruction Manual.

68. R.E. Steele, W.E. Walker, D.E. Burge and H.C. Ehrmantrant, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (1963).

69. Ditchburn Proc. Roy. Soc., 236 217 (1956).

70. Massey and Potter, "Atmospheric Photochemistry" (R.I.C. Monograph, 1 2 (1961).

71. W.A. Noyes and P.A. Leighton, "The Photochemistry of Gases", Reinhold, pp.82-134, (1941).

72. M. Fineman and S.D. Ross, J. Polym. Sci., 5 259 (1950).

73. A. Scotney and A. M^{c}Caskie, Private Communication.

74. I.C. M^{c}Neill, J. Polym. Sci., A4 2479 (1966).

75. A. Charlesby and S.H. Pinner, Proc. Roy. Soc., A249 367 (1959).

76. Polymer Handbook, Brandrup and Immergut (Eds.) Interscience, New York (1966).

77. N. Grassie and I.C. M^{c}Laren Unpublished.

78. N. Grassie and A.J. Davidson In Preparation.

79. N. Grassie and E. Farish, Eur. Polym. J. 3 627 (1967).

80. N. Grassie and E. Farish, Eur. Polym. J. 3 305 (1967).

81. N. Grassie and N.A. Weir, J. Appl. Polym. Sci., 9 963,975,987,999 (1965).

82. A.R. Shultz, J. Polym. Sci., 47 267 (1960).